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INDUSTRIAL PROCESS PROFILES FOR ENVIRONMENTAL USE: Chapter 16. The Fluorocarbon-Hydrogen Floride Industry

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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16. ABSTRACT

The catalog of Industrial Process Profiles for Environmental Use was developed as an aid in defining the environmental impacts of industrial activity in the United States. Entries for each industry are in consistent format and form separate chapters of the study. The materials of the fluorocarbon-hydrogen fluoride industry consist primarily of chemically and thermally stable organofluoro compounds which generally have nontoxic and nonflammable qualities. The industry is discussed in two segments: (1) Fluorocarbon Production and (2) Hydrogen Fluoride Production. One chemical tree, fourteen process flow sheets and twenty-nine process descriptions have been prepared to characterize the industry. Within each process description available data have been presented on input materials, operating parameters, utility requirements and waste streams. Data related to the subject matter, including company, product and raw material data, are included as appendices.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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INDUSTRIAL PROCESS PROFILES

FOR ENVIRONMENTAL USE

CHAPTER 16

THE FLUOROCARBON-HYDROGEN FLUORIDE INDUSTRY

by

Dow Chemical U.S.A.
Michigan Division
Midland, Michigan

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FLUOROCARBONS - HYDROGEN FLUORIDE INDUSTRY

INDUSTRY DESCRIPTION

The materials of the fluorocarbon-hydrogen fluoride industry consist primarily of chemically and thermally stable organo-fluoro compounds which generally have nontoxic and nonflammable qualities. Most of the fluorocarbons are aliphatic compounds, although recently there has been an increased interest in the use of aromatic fluorocompounds.

The industry is composed of two major segments. One segment is the production of hydrogen fluoride for use as a raw material. Another segment involves reacting the hydrogen fluoride with raw materials to form the fluorocarbon products.

As shown on the process flowsheets, the raw materials of this industry are primarily chlorocarbons, such as carbon tetrachloride and chloroform, and anhydrous hydrogen fluoride. The bulk of the products from this industry is formed by allowing the chloro-carbons and hydrogen fluoride to react in the liquid or vapor phase or in an electrochemical cell; the fluorocarbons and hydrogen chloride are the usual products.

Fifteen different companies manufacture fluorocarbons at 23 locations. The manufacturing facilities vary in size from 50 kg to 50 million kg per year. An estimated 450 million kg of fluoro-carbon compounds are produced annually in this industry.

The manufacturing locations of this industry are primarily throughout the eastern, midwestern, and southern parts of the U.S. Many of these facilities are located near large cities and most are associated with other industries at that same location.

The growth rate of the industry from 1963 to 1973 averaged nearly 9% per year. A growth rate of 6.5% per year through 1977 was projected in January 1973. However, with increasing regulatory pressure being exerted due to the possible health and safety hazards of aerosol sprays, the current projected growth rate is nearer 4-5% per year for the next five years.

The hydrogen fluoride (HF) used in the fluorocarbon industry is generated to a large extent by the fluorocarbon producers primarily for use in this industry, and approximately 45% of the HF made in the U.S. is so used. The HF industry is therefore considered part of the fluorocarbon industry. Another 38% of the HF is used in the aluminum industry for the production of sodium aluminum fluoride, synthetic cryolite. Lesser amounts are used for petroleum refining (5-6%), stainless steel pickling (3-4%), uranium hexafluoride for nuclear fuels (2-3%) and other minor applications.

Hydrogen fluoride (HF) is generated from the reaction between sulfuric acid and acid grade (≥97%) fluorspar (CaF_2) and is the sole major product of this segment of the fluorocarbon industry. The bulk of the hydrogen fluoride is manufactured in the anhydrous state. If hydrofluoric acid is desired, the anhydrous material is dissolved in water. Ten different companies manufacture hydrogen fluoride at 14 locations. The manufacturing facilities vary in size from 4000 to 98,000 metric tons/year. A total of 350,000 metric tons of hydrogen fluoride is produced annually from 1,220,000 metric tons of fluorspar.

Raw Materials

The raw materials used for the production of hydrogen fluoride are sulfuric acid and fluorspar (97% CaF_2). Most of the fluorspar is mined in Mexico, Canada, and Europe; a small amount is mined in Illinois and a few other states. Fluorspar usually occurs as

veins associated with limestone and sandstone, but is sometimes associated with galena, sphalerite, calcite, or barite.

The major chlorocarbon raw materials used in this industry are carbon tetrachloride, chloroform, and tetrachloroethylene - products of the Industrial Organic Chemicals Industry. Since the reactions to produce the fluorocarbons are carried out in closed systems, there is minimum danger from the chlorocarbons, although some of these raw materials are toxic at high concentrations. The basic raw materials are given in Appendix A.

Products

The industry began with the discovery that certain fluorocarbons make excellent refrigerants. The production of refrigerants and aerosols currently constitutes approximately 75% of total production. Other applications include solvents, blowing agents for plastic foam (10%), feedstocks for fluoropolymers (5%) and fire extinguishants. The two most important products of this industry are trichlorofluoromethane and dichlorodifluoromethane (fluorocarbon 11 and 12, respectively) with a combined production of approximately 80% of the total. Excluded from examination in this study are fluorocarbon compounds marketed primarily as pharmaceutical products, insecticides, surfactants, explosives, dyes and intermediates. A list of products of this industry as defined is given in Appendix B.

Companies

The major companies in this industry are some of the largest chemical manufacturing companies in the U.S. These include:

Allied Chemical Corporation
E.I. du Pont de Nemours & Co., Inc.
Kaiser Aluminum and Chemical
Penwalt Corporation

Racon, Inc.
Union Carbide Corporation

Appendix C gives a comprehensive company listing.

Environmental Impact

Most of the solid wastes from this industry are buried in the ground. The liquid products are usually scrubbed with water or aqueous castic and dried with a desiccant. The liquid wastes can be neutralized and sent to a waste pond or stream.

A large quantity of hydrogen chloride by-product is normally produced in the anhydrous gaseous state. This is usually transferred to other plant uses. Aqueous hydrochloric acid can also be transferred and is rarely discarded.

Gaseous fluorocarbon emissions during manufacture and processing are kept to a minimum by the industry. However, the users of many of these products do allow them to escape into the atmosphere. Measurements of the effect of these gases on our environment are incomplete at present.

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INDUSTRY ANALYSIS

The data presented herein are taken primarily from the patent literature. Ancillary data are taken from recent trade publications, related books, and company brochures. Much of the thermal data on the heating or cooling requirements for processes had to be calculated and/or estimated since this information was not available in the literature. Due to the present economic climate and the potential fluorocarbon-ozone problem, actual production data presented may vary from the reported values.

Other variations in production data may be caused by improvements in processing techniques since the data were printed. This, of course, would be considered as a trade secret by the manufacturing companies, and there is no open access to this information. Research findings also play a role in the quantities of certain fluorocarbons being manufactured. For example, production of aromatic fluorocarbons was recently begun due to new applications or uses. While production is very small now, it may continue to grow and expand in the future.

The industry has been divided into two segments for analysis: Fluorocarbon Production and HF Production. Process flowsheets and process descriptions are given for the processes involved in these segments of the industry with operating parameters, input materials, utilities, and waste streams defined for each process.

In general, manufacturing companies treat production techniques as proprietary information and are reluctant to divulge specific information relating to methods used. The process descriptions contained in this section reflect data for selected reactions considered typical for fluorocarbon production. The reader must

be aware that, in some cases, the reaction specified may not be the method of choice for commercial production of the indicated fluorocarbon, or may be one of several alternate routes to the product.

Producer/product data compiled from the 1976 Directory of Chemical Producers differs somewhat from data received from producers and from industry experts. Limited attempts to resolve this inconsistency were unsuccessful. The data are presented as compiled, with footnoes to indicate inconsistencies.

FLUOROCARBON PRODUCTION PROCESSES

The primary raw materials for the preparation of the principal fluorocarbons are the chlorocarbons. Certain fluorocarbons are also prepared from acetylene. Many of the incompletely fluorinated products are subjected to additional chemical reactions (processes) to give other useful products.

Chemical trees shown in Figure 1 illustrate the sequences of reactions in which fluorocarbons are prepared from hydrocarbon raw materials. Table 1 lists the process descriptions given for this segment.

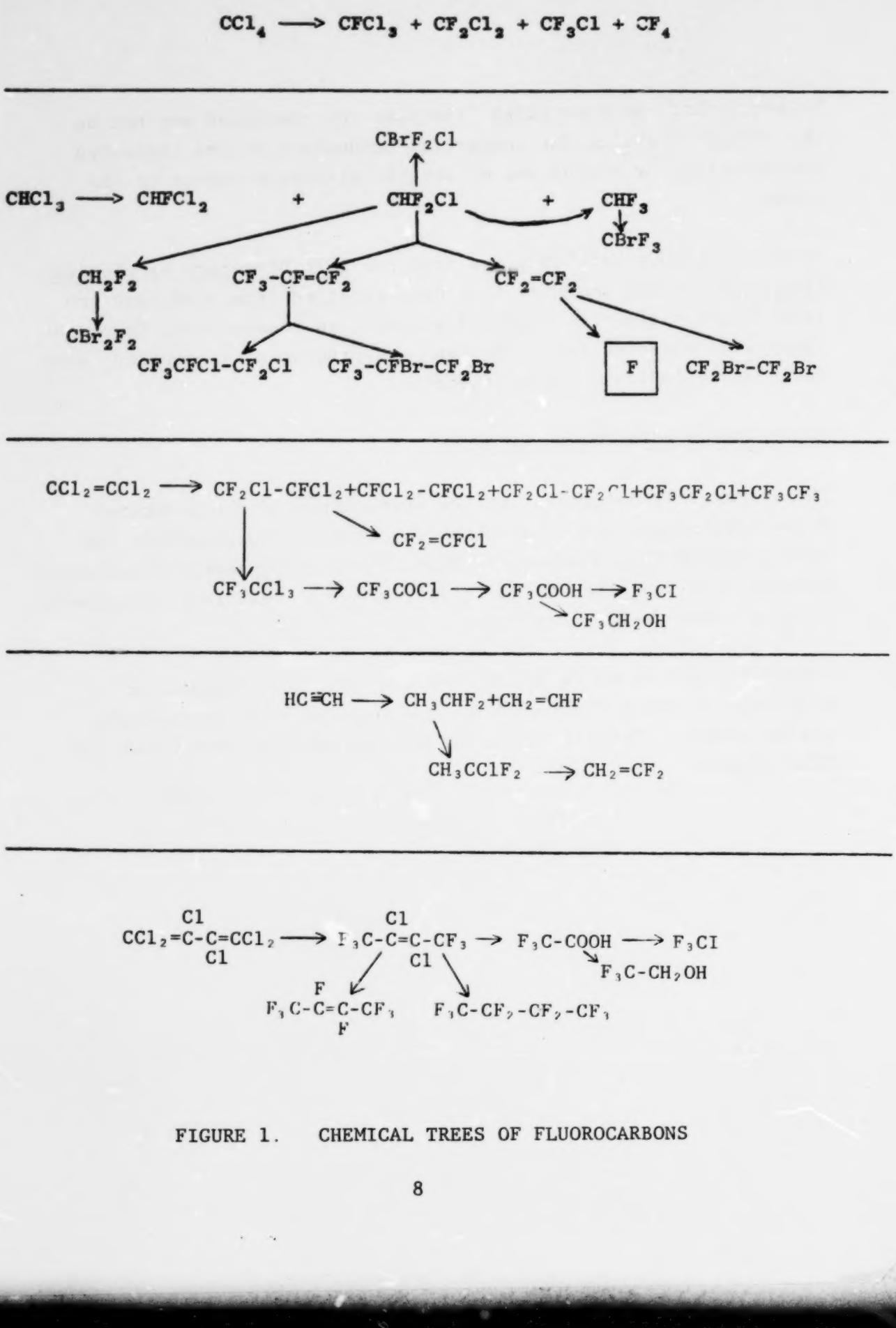

FIGURE 1. CHEMICAL TREES OF FLUOROCARBONS

Table 1. PROCESS DESCRIPTIONS FOR FLUOROCARBON PRODUCTION

1.	Liquid Phase Fluorination
2.	Distillation from Liquid Phase Fluorination
3.	Separation, Neutralization, Drying of Products from Liquid Phase Fluorination
4.	Vapor Phase Fluorination
5.	Distillation from Vapor Phase Fluorination
6.	Separation, Neutralization, Drying of Products from Vapor Phase Fluorination
7.	Electrochemical Fluorination
8.	Separation, Neutralization, Drying of Products from Electrochemical Fluorination
9.	Bromination of Fluorohydrocarbons
10.	Purification of Bromofluorocarbons
11.	Pyrolysis of Chlorodifluoromethane
12.	Pyrolysate Scrubber, Separator, Drier
13.	Reductive Dechlorination of 1,1,2-Trichlorotrifluoroethane
14.	Separation and Purification of Products from Dechlorination of 1,1,2-Trichlorotrifluoroethane
15.	Addition of Halogens to Perfluoroalkenes
16.	Dimerization of Fluoroolefins
17.	Oxidation of Chlorofluoroolefins
18.	Production of Fluoroalcohols by Catalytic Hydrogenation
19.	Preparation of Perfluoroalkyl Iodides
20.	HF Addition to Acetylene
21.	Separation and Purification of Fluorohydrocarbons from HF Addition
22.	Chlorination of 1,1-Difluoroethane
23.	Dehydrochlorination of 1-Chloro-1,1-difluoroethane
24.	Production of Fluoroaromatic Compounds

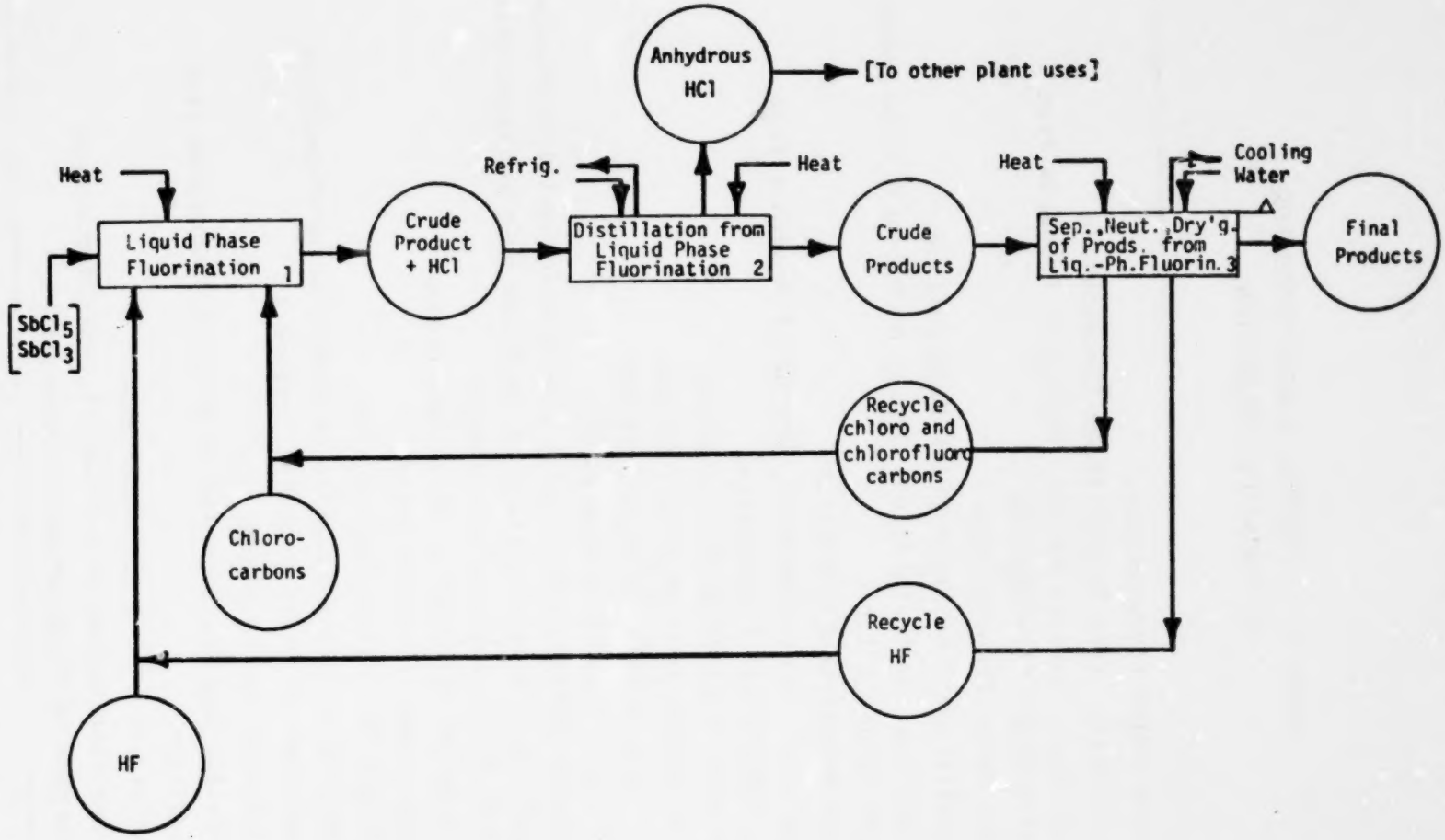

FIGURE 2. FLOWSHEET FOR PRODUCTION OF FLUOROCARBONS BY LIQUID PHASE FLUORINATION

FLUOROCARBON PRODUCTION PROCESS NUMBER 1

Liquid Phase Fluorination

1. Function

To convert chlorocarbons to fluorocarbons by means of fluorination with anhydrous hydrogen fluoride together with a catalyst. The reactor may be made of steel, various stainless alloys, Monel or nickel clad steel.

a. Carbon tetrachloride is converted into dichlorodifluoromethane (FC-12) and trichlorofluoromethane (FC-11).

b. Chloroform is converted into chlorodifluoromethane (FC-22) and dichlorofluoromethane (FC-21).

c. Tetrachloroethylene and chlorine are converted into trichlorotrifluoroethane (FC-113), tetrachlorodifluoroethane (FC-112), and dichlorotetrafluoroethane (FC-114).

d. Hexachlorobutadiene is converted into 2,3-dichlorohexafluorobutene-2. Perfluorobutene-2, and perfluorobutane are made from 2,3-dichlorohexafluorobutene-2 by subsequent and different reactions.

2. Input Materials

Assuming a production capabity of 68 million kg of product per year, and a production rate of one kg of product per kg of catalyst per hour, the quantities of raw materials required for (a) above are:

CCl_4---------	9798 kg/hr
HF ---------	2077 kg/hr

for (b) above:

$CHCl_3$	---------	13066 kg/hr
HF	---------	2077 kg/hr

and for (c) above:

$CCl_2=CCl_2$	-----	7610 kg/hr
HF	---------	4500 kg/hr
Cl_2	---------	3250 kg/hr

Since the process can be operated to prepare more of one product than another, the feed ratio of HF to chlorocarbon may vary depending upon what product is desired.

The catalyst consists of 2885 kg $SbCl_5$, 290 kg $SbCl_3$ and 7938 kg CCl_3F. The efficiency of HF utilization is estimated to be 97% and that of CCl_4 is estimated to be 95-98%.

3. Operating Parameters

Satisfactory operating conditions cover wide ranges. The pressures may vary from 0 to 35 kg/cm^2, the temperatures from 45-200°C, catalyst concentrations from 10 to 90 weight per cent, and product take-off temperatures from -30° to +100°C. A typical example uses CCl_4 and HF, a pressure of 7 kg/cm^2, a reactor temperature of 80°C, a catalyst concentration of 60 weight percent in CCl_3F (400 parts $SbCl_5$, 40 parts $SbCl_3$, 660 parts CCl_3F), and a reflux condenser temperature set at -5°C. Under these conditions, the products will consist primarily of CHl and CCl_2F_2 (all CCl_4 and CCl_3F being returned to the reactor). Increasing the reflux condenser temperature to +5°C allows some of the CCl_3F to escape to form a 9:1 ratio of CCl_2F_2 to CCl_3F. An increase in pressure will allow an increase in condenser temperatures without altering the product composition. Thus, a range of variables is possible without a change in product composition. In general, an increase in temperature and pressure will result in an increase in rate.

Based on a plant having a production capacity of 68 million kg of product per year, and a production rate of one kg of product per kg catalyst per hour, the catalyst bed size is estimated to be 1 meter^2 x 6 meters.

4. Utilities

The reactor is normally heated by steam to a temperature of 80°C. Assuming again a production capacity of 68 million kg of product per year and a production rate of one kg of product per kg of catalyst per hour, for conversions (a), (b), and (c) above:

(a) Approximately 400,000 kcal of heat per hour are required.
(b) " 740,000 " " " " " " " .
(c) " 280,000 " " " " " " " .

5. Waste Streams

The reaction is carried out in a closed system--the only discharges to air or water would be due to leaks and spills. Estimated catalyst losses: 2×10^{-4} kg/kg product. The waste catalyst can be disposed of by burial.

6. EPA Source Classification Code

7. References

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FLUOROCARBON PRODUCTION PROCESS NUMBER 2

Distillation from Liquid Phase Fluorination

1. Function

To separate more volatile by-products from the feed and product materials and to return the catalyst to the fluorination step. Since the by-product is anhydrous hydrogen chloride, steel or stainless steel alloys may be used.

2. Input Materials

Depending upon the product desired, anhydrous hydrogen chloride, chlorocarbons, chlorofluorocarbons, and hydrogen fluoride are present as the feed. Also small traces of the antimony salts may be present in the feed.

If one assumes that an average of two chlorines per molecule are replaced by fluorines, then for a plant having a production capacity of 68 million kg per year, between 3600 and 8000 kg/hr of anhydrous HCl would be formed, depending upon what product is desired.

3. Operating Parameters

As indicated in the fluorination process, the higher the pressure, the higher the distillation temperature may be. The actual temperature and pressure used also depend upon what product(s) is desired. The temperature can thus be varied from -30° to +100°C and the pressures can be varied from 3 to 14 kg/cm^2.

4. Utilities

The temperature at which the distillation is performed determines the type of cooling required. When the distillation is performed at temperatures below 20°C, conventional

refrigeration cooling is required. Above 40°C, water cooling will be adequate. On the above size plant, approximately 500 kcal/hr of heat must be withdrawn.

5. **Waste Streams**

No emissions should occur in this process. All anhydrous HCl is recovered and used in other plant processes. Because this is a pressurized system, leaks may develop.

6. EPA Source Classification Code

3-01-011-01 BY-Product w/o SCRUB

7. References

1) Stacey, M., Tatlow, J. C., and Sharpe, A. G., Editors, "Advances in Fluorine Chemistry," Vol. 3, Butterworths, Washington, DC, 1963, pp 117-180.

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Separation, Neutralization, Drying of Products from Liquid Phase Fluorination

1. Function

   a. To separate the crude products into the desired final products and recycle materials.

   b. To neutralize any acidic materials that may be present in the final products.

   c. To dry the final products prior to end use.

   The separation step is usually divided into two steps, distillation and decantation. Steel or stainless steel materials of construction may be used.

2. Input Materials

   Chlorocarbons, chlorofluorocarbons and anhydrous HF feed into this process. The quantities of these materials used depend upon what product is desired. For example, if one wishes to produce equal amounts of CCl_2F_2 and CCl_3F as products, then CCl_4 is fluorinated under conditions such that these two materials are produced in nearly equal amounts. Along with this, a small amount (~5%) of unreacted CCl_4 and HF also are fed. This mixture of feed materials is subjected to an azeotropic distillation, during which time the CCl_2F_2 and HF are removed from the CCl_3F and CCl_4.

   The azeotrope, CCl_2F_2 and HF, is then separated further by decantation and the CCl_2F_2 containing a trace of HF is washed, e.g., by aqueous caustic, then dried, e.g., by molecular sieves, silica gel, etc., and bottled. Depending upon the end

use, an additional distillation may be performed. The decanted HF is recycled to the fluorination process step (process 1).

If CCl_2F_2 is the only product desired, the CCl_3F and CCl_4 are recycled back to the fluorination process. If CCl_3F is also desired as a product, it may be separated from CCl_4 by distillation. Neutralization and drying of CCl_3F is performed, as in the case of CCl_2F_2.

Assuming a production capacity of 68 million kg of product per year and assuming that equal productions of CCl_2F_2 and CCl_3F are desired, about 4200 kg of each of these materials, along with 260 kg of CCl_4 and 25 kg of HF, per hour are fed into this process.

3. Operating Parameters

Again assuming that equal productions of CCl_2F_2 and CCl_3F are desired as products, the separation by azeotropic distillation may be performed under a variety of pressures and temperatures. Since the pressure and temperature are directly related to each other, more pressure will allow an increase in temperature to be used and hence less condenser cooling required. However, at higher temperatures CCl_2F_2 dissolves to a greater extent in HF and HF is also more soluble in CCl_2F_2. The conditions for separating this azeotrope by decantation will probably be chosen by the manufacturer based on cooling capacity, materials of construction, etc.

4. Utilities

Steam requirements for separation by distillation will vary depending upon what product(s) is desired. Assuming a production of 4200 kg per hour of CCl_2F_2, an estimated 170,000 kcal/hr

of heat are required for the distillation. Only a small quantity of heat is required for regeneration of the (molecular sieve) drying agent.

5. Waste Streams

For neutralization of the <1% of the HF present in the CCl_2F_2 following decantation, aqueous caustic may be used. Up to 20 kg/hr of NaOH may be required for neutralization. The spent caustic (NaF + NaOH) may be discharged to a pond and completely neutralized.

6. EPA Source Classification Code

None established.

7. References

1) Stacey, M., Tatlow, J. C., and Sharpe, A. G., Editors, "Advances in Fluorine Chemistry," Vol. 3, Butterworths, Washington, DC, 1963, pp 117-180.

2) Benning, A. F., U.S. Patent 2,450,415 (1948).

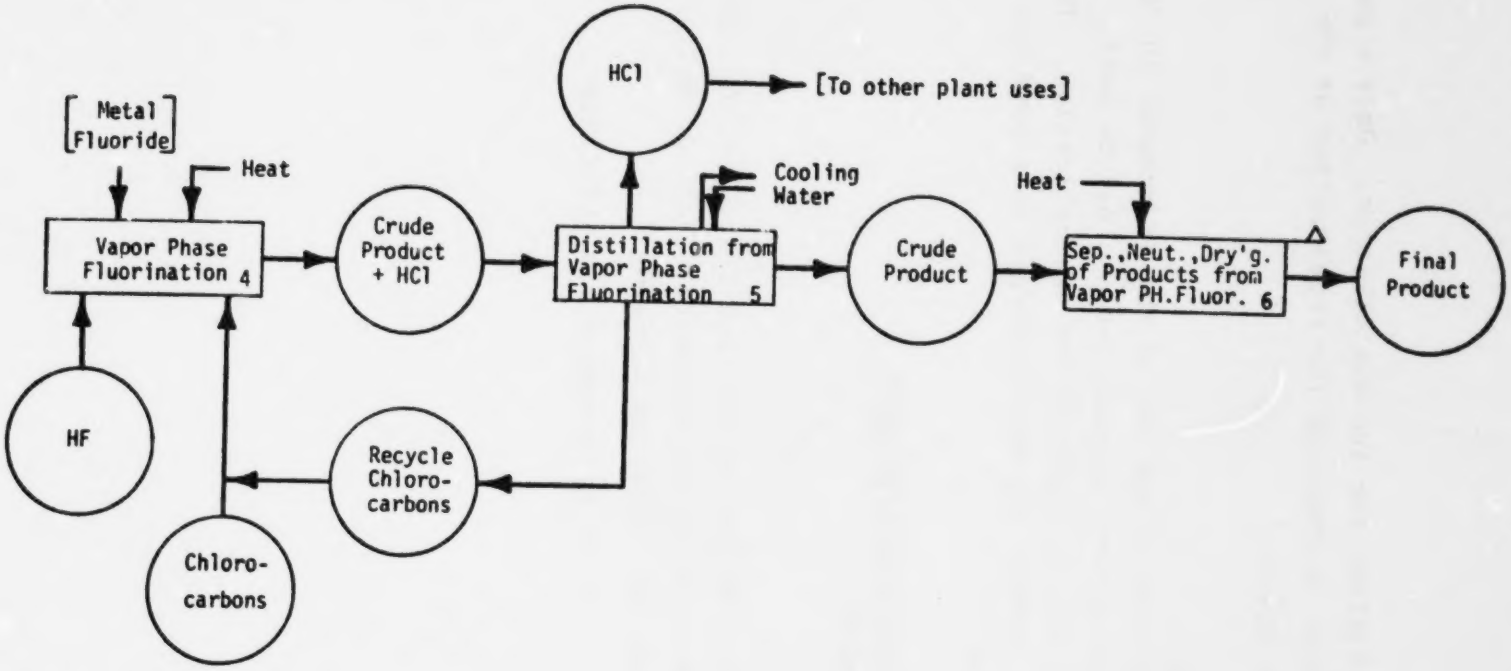

FIGURE 3. FLOWSHEET FOR PRODUCTION OF FLUOROCARBONS BY VAPOR PHASE FLUORINATION

Vapor Phase Fluorination

1. Function

To convert chlorocarbons to fluorocarbons by means of vapor phase fluorination with anhydrous hydrogen fluoride and a catalyst.

Any of a number of chlorocarbons is converted into a number of fluorocarbons. In this process (as opposed to the liquid phase fluorination process) less control on the degree of fluorination is possible; therefore, a larger mixture of products is obtained. In general, this process is more suitable for producing the more highly fluorinated compounds.

The reactor consists of a heated tube or series of tubes filled with a granular catalyst and fed by a vaporized mixture of the chlorocarbon and anhydrous hydrogen fluoride. A variety of metallic fluorides may be used as catalysts. These may be in a solid granular or supported form. The reactor can be made of steel, stainless steel, or clad or alloy steel.

2. Input Materials

The quantities and types of materials fed into this process vary considerably and are dependent upon the product(s) desired. The normal mole ratio of HF to chlorocarbon is 1.1 to 1.5 and the efficiency of HF utilization is usually from 90 to 100%.

A representative list of chlorocarbons which can be converted into fluorocarbons is given below.

Table 2. FLUOROCARBONS PRODUCED FROM CHLOROCARBONS

Feed	Products
CCl_4	CCl_3F, CCl_2F_2, $CClF_3$, CF_4
$CHCl_3$	$CHCl_2F$, $CHClF_2$, CHF_3
CCl_2-CCl_2 + Cl_2	CCl_2F-$CClF_2$, $CClF_2$-$CClF_2$, $CClF_2$-CF_3 CF_3-CF_3
CCl_3-$\overset{O}{\overset{\|}{C}}$-$CCl_3$	$CClF_2$-$\overset{O}{\overset{\|}{C}}$-$CClF_2$, $CClF_2$-$\overset{O}{\overset{\|}{C}}$-$CF_3$, CF_3-$\overset{O}{\overset{\|}{C}}$-$CF_3$
CBr_4	$CBrF_3$, CHF_3, CBr_2F_2, CBr_3F
CH_2Cl_2	CH_2F_2, CH_2ClF

Assuming a production capacity of 10 million kg of product per year, and assuming that approximately equal amounts of CCl_2F_2 and CCl_3F are desired from CCl_4, the quantities of raw materials required are:

CCl_4 --------	1400 kg/hr
HF ----------	300 kg/hr

With this ratio of feed, the following quantities of products would probably be obtained:

CCl_2F_2 ------	640 kg/hr
CCl_3F -------	480 kg/hr
$CClF_3$ -------	13 kg/hr
HCl ---------	525 kg/hr

3. Operating Parameters

The temperature employed will vary from 100° to 500°C. The fluorination is usually carried out at about atmospheric pressure (1 kg/cm^2). Typical catalysts which may be used are

chromium oxyfluoride, chromium oxyfluoride - aluminum fluoride, AlF_3, ZrF_4, CrF_3, etc. Depending upon what production quantity is desired, the size of the reactor will vary. A typical example is seen in the following:

A total of 208 g of CCl_4 and 36 g of HF was vaporized and passed through a 5 x 30 cm bed of 0.5 x 0.5 cm pellets of chromium oxyfluoride in a nickel reactor for 30 min. at 550°C and a contact time of 6.6 sec. The products consisted of 9.6% $CClF_3$, 40.9% CCl_2F_2, 13.6% CCl_3F, and 5.9% CCl_4. In general, at any one temperature, a decrease in contact time produces smaller quantities of the highly fluorinated materials and an increase in temperature produces greater quantities of the highly fluorinated materials.

4. Utilities

The reactor is heated by flue gas or by high pressure steam to a temperature of about 150°C. Assuming a production capacity of 10 million kg of product per year, a total of about 2 million kcal of heat per hour is required. In addition to this, about 450 kWh of electrical energy are required.

5. Waste Streams

Waste streams should be limited to leaks and spills from this closed system process.

6. EPA Source Classification Code

None established.

7. References

1) Stacey, M., Tatlow, J. C., and Sharpe, A. G., Editors, "Advances in Fluorine Chemistry," Vol. 3, Butterworths, Washington, DC, 1963, pp 117-180.

2) Ruh, R. P. and Davis, R. A., U.S. Patent 2,745,886 (1956).

3) Foulletier, L., and Dassaud, R., U.S. Patent 2,897,064 (1959).

4) Davis, R. A., and Brcadworth, M. R., U.S. Patent 3,002,934 (1961)

5) Farbwerke Hoechst A.-G., Fr. Patent 1,343,392 (1963).

6) Swamer, F. W., Fr. Patent 1,372,549 (1964).

Distillation from Vapor Phase Fluorination

1. Function

To separate the products obtained from the vapor phase fluorination process. The still may be made of steel, stainless steel, or nickel clad steel.

2. Input Materials

The feed to this process consists of anhydrous hydrogen chloride, chlorofluorocarbons, fluorohydrocarbons, chlorocarbons, and small quantities of anhydrous hydrogen fluoride. The products may be separated by low temperature fractional distillation after separating out the anhydrous HCl. However, certain fluorinated products may have a boiling point very close to that of HCl. In this case, the HCl and fluorocarbon may be scrubbed with water, dissolving the HCl. One of the by-products from this process is frequently a 30% HCl solution.

If conditions are adjusted during the fluorination step such that no fluorocarbons are formed which have the same boiling point as HCl, the HCl may be first separated and the remaining fluorocarbons separated as in the liquid phase fluorination process (see process 3).

3. Operating Parameters

If the process is operated such that the anhydrous HCl is the only highly volatile product, the operating conditions may be the same as the distillation performed in process 2. However, if a volatile fluorocarbon also is formed, then the HCl may be scrubbed with water and the volatile (insoluble) fluorocarbon recovered from the aqueous HCl. In this case, the distillation may be accomplished under less pressure, i.e., up to atmospheric pressure.

Thus, the pressure, temperature, and refrigeration required for the distillation depend entirely upon the product feed, the temperature, and the contact time for fluorination.

4. Utilities

The quantity of refrigeration needed here is similar to that in process 2, assuming similar input materials. Under the proper conditions, water cooling would be adequate.

5. Waste Streams

No waste streams are involved in the above distillation. The scrubbed HCl may be removed to other plant uses as a 30% solution.

6. EPA Source Classification Code

3-01-011-02 BY-PRODUCT w/SCRUB

7. References

1) Stacey, M. , Tatlow, J. C., and Sharpe, A. G., Editors, "Advances in Fluorine Chemistry," Vol. 3, Butterworths, Washington, DC, 1963, pp 146-154.

2) Slesser, C., Editor, "Preparation, Properties, and Technology of Fluorine and Organic Fluoro Compounds," McGraw-Hill Book Company, Inc., New York, 1951, pp 427-454.

3) Ruh, R. P., and Davis, R. A., U.S. Patent 2,745,886 (1956).

Separation, Neutralization, Drying of Products from Vapor Phase Fluorination

1. Function

To separate, neutralize, and dry all desired products prepared in the vapor phase process. Prior to this process, the HCl and low boiling products were removed via distillation (see process 5). The remaining fluorocarbons, chlorofluorocarbons, and fluorohydrocarbons along with small quantities of HF are separated by distillation, neutralized by scrubbing with aqueous caustic to eliminate the HF, and dried with molecular sieves, silica gel, etc. The still can be made from steel, stainless steel, or similar materials.

2. Input Materials

The feed materials to this process vary considerably depending on what products are being made. However, a typical example may be seen below:

Assuming a production capacity of 10 million kg of product per year, and assuming that nearly equal amounts of CCl_2F_2 and CCl_3F are desired, the quantities of input materials are:

CCl_2F_2	650 kg/hr
CCl_3F	490 kg/hr
HF	3 kg/hr

3. Operating Parameters

High efficiency distillation columns may be used to separate the products from this process. They can be operated under pressure, but usually are operated at atmospheric conditions. However, for feeds such as CCl_2F_2 and CCl_3F, the same operating

conditions may be used as given in process 3. For other feeds, the distillation will be carried out at different temperatures. The temperatures employed will be dependent upon the boiling points of products being separated.

4. Utilities

Steam requirements for this process will vary considerably depending upon what products are being separated. Assuming the production of 650 kg/hr of CCl_2F_2 and 490 kg/hr of CCl_3F, an estimated 48,000 kcal/hr of heat are required for the distillation.

5. Waste Streams

A small amount of aqueous NaF - NaOH will be obtained from the caustic scrubbing of the fluorocarbons. This may amount to about 7 kg/hr for the production quantities given above. This can be completely neutralized and disposed of by burial.

6. EPA Source Classification Code

None established.

7. References

1) Stacey, M., Tatlow, J. C., and Sharpe, A. G., Editors, "Advances in Fluorine Chemistry," Vol. 3, Butterworths, Washington, DC, 1963, pages 146-154.

2) Slesser, C., Editor, "Preparation, Properties, and Technology of Fluorine and Organic Fluoro Compounds," McGraw-Hill Book Company, Inc., New York, 1951, pages 427-454.

3) Ruh, R. P., and Davis, R. A., U.S. Patent 2,745,886 (1956).

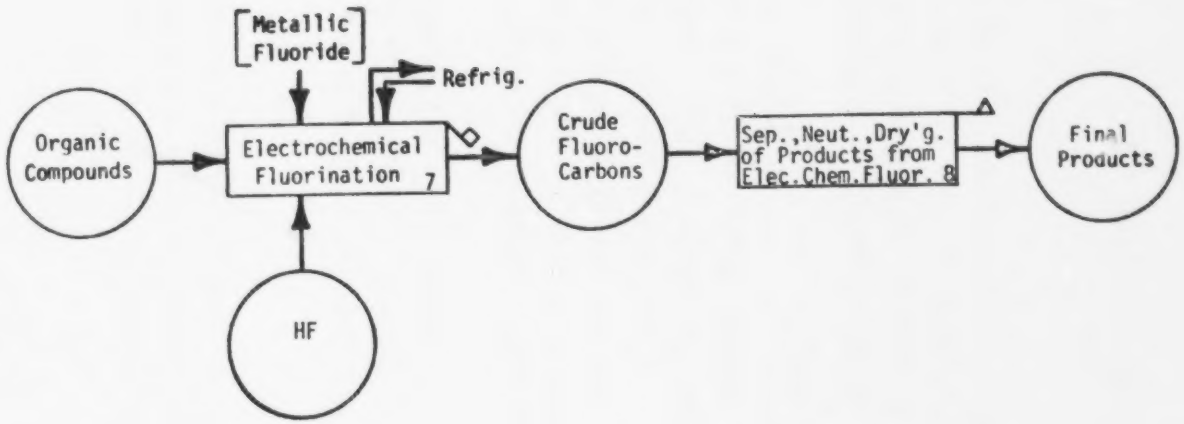

FIGURE 4. FLOWSHEET FOR THE PRODUCTION OF FLUOROCARBONS BY ELECTROCHEMICAL FLUORINATION

Electrochemical Fluorination

1. Function

To convert hydrocarbons and chlorocarbons into fluorocarbons. Many organic compounds containing ether, carboxyl, amine, or other groups can be fluorinated by this process without destroying these groups. Other fluorination processes do not permit this.

The electrochemical cell usually consists of a single compartment cylindrical or rectangular metal vessel, commonly made of iron, steel, or nickel. A condenser made of iron or copper is attached to the cover, and is operated in a manner to return the effluent hydrogen fluoride to the electrochemical cell while allowing the products to exit the cell.

Products which boil at high temperatures are frequently drawn off the bottom of the cell through a valve. (Most completely fluorinated species are insoluble in liquid HF.)

2. Input Materials

Feed to the cell consists of a large variety of hydrocarbons, chlorohydrocarbons, and organic materials containing functional groups. Typical feeds and products are listed in Table 3.

Table 3. INPUT MATERIALS AND PRODUCTS FROM ELECTROCHEMICAL FLUORINATION

Feed	Product
Hexanes	Perfluorohexanes
CH_3-O-CH_3	CHF_2-O-CF_3, CF_3-OCF_3, CHF_2-O-CHF_2
CH_3COF	CF_3COF
CH_3SO_2F	CF_3SO_2F
CH_2Cl_2	CCl_2F_2, $CHCl_2F$
$CHCl=CCl_2$	$CHClF-CCl_2F$
$(C_4H_9)_3N$	$(C_4F_9)_3N$
$(CH_3CO)_2O$	CF_3COF

In addition to the organic materials, anhydrous liquid hydrogen fluoride and usually a metallic fluoride, e.g., sodium fluoride or lithium fluoride, are added.

3. **Operating Parameters**

During electrolysis, anhydrous HF is added periodically to keep the cell full. The optimum cell potential is below 10 v and is usually around 5 v. Normally, direct current is used, although alternating current is effective. The current controls the amount of fluorination that takes place in a given time. For any given cell the potential applied and the substrate concentration are the variables which determine current density. Current densities usually range from 0.0008 to 0.02 amps/cm^2. Current efficiencies range from 60 to 90%.

The temperature at which electrochemical fluorinations are carried out usually ranges from -10 to +40°C, but most frequently it is aroung 0°C. Normally the fluorinations are

performed at atmospheric pressures, but higher pressures are required when the temperature is above 40°C.

Concentrations of the substrate may vary from 1 to 15%. Normally the substrate is added continuously at the rate it is fluorinated.

The optimum conditions for fluorination will usually be chosen so that the best yields are obtained of the desired products. Yields vary considerably and are low for many compounds.

Cell sizes have been designed from 10 to 10,000 amps. With all the ancillary equipment a cell 23 cm by 8.5 cm, and holding about 1 ℓ. of solution, was rated at 20 amps. It measured 1.3 x 1.3 x 0.6 meters. The size of the cell will obviously depend upon what quantities of product are desired.

4. **Utilities**

The major kind of energy required in this process is electrical and the amount will depend upon the degree of fluorination, as well as the quantity of materials produced. From 0.4 to 0.6 g of fluorine are available per amp hr. Refrigeration is required for the condenser. The amount of cooling required will depend to a large degree on the temperature at which the cell is operated which, in turn, depends upon what substrate is being fluorinated. Because of the high energy demands, on site power generation is usually from oil or gas fired turbogenerators.

5. **Waste Streams**

There are almost no discharges to the air, water, or ground in this process. Any HF which escapes from the condenser is

absorbed by NaF. The NaF·HF may be heated to drive off the HF and regenerate the NaF, or it may be disposed of by burial.

6. EPA Source Classification Code

None established.

7. References

1) Stacey, M., Tatlow, J. C., and Sharpe, A. G., Editors, "Advances in Fluorine Chemistry," Vol. 1, Butterworths, Washington, DC, 1960, pages 129-165.

2) Simons, J. H., Editor, "Fluorine Chemistry," Vol. 1, pages 414-420, Vol. 2., pages 340-341, Academic Press, Inc., New York (1950).

3) Wolfe, J. K., U.S. Patent 2,806,817 (1957).

Separation, Neutralization, Drying of Products from Electrochemical Fluorination

1. Function

To separate, neutralize, and dry all desired products prepared in the electrochemical fluorination process. Because the products will contain compounds which vary considerably in their degree of fluorination, their separation may at times require high efficiency distillation columns.

2. Input Materials

All products and by-products from the electrochemical fluorination (see process 7) are fed into this process. When acid fluorides or anhydrides are the products, they are scrubbed with sodium fluoride to eliminate any HF. Fluorinated hydrocarbons, ethers, amines, etc. are scrubbed with water or aqueous caustic and the wet products are dried with a desiccant.

3. Operating Parameters

The products are usually cooled, compressed, and distilled under pressure; however, the degree of cooling and compressing required will depend largely on the product obtained since many of these are liquid under normal conditions. Operating pressures may be as high as 20 kg/cm^2 and temperatures as low as -25°C.

4. Utilities

It is estimated that between 1 and 20 kcal/mole of heat are required for the distillation of the products. If refrigeration is used, 5-50 kcal/mole of heat need to be withdrawn from the system.

5. Waste Streams

A small amount (<10 g/kg product) of sodium fluoride·HF or aqueous NaF/NaCl will be discharged to a waste pond. Small amounts of fluorocarbons may be discharged to the air in the pressurized distillation step.

6. EPA Source Classification Code

None established.

7. References

1) Stacey, M., Tatlow, J. C., and Sharpe, A. G., Editors, "Advances in Fluorine Chemistry," Vol. 1, Butterworths, Washington, DC, pages 129-165 (1960).

2) Simons, J. H., Editor, "Fluorine Chemistry," Vol. 1, Academic Press, Inc., New York, 1950, pages 414-420, Vol. 2, pages 340-341.

3) Wolfe, J. K., U.S. Patent 2,806,817 (1957).

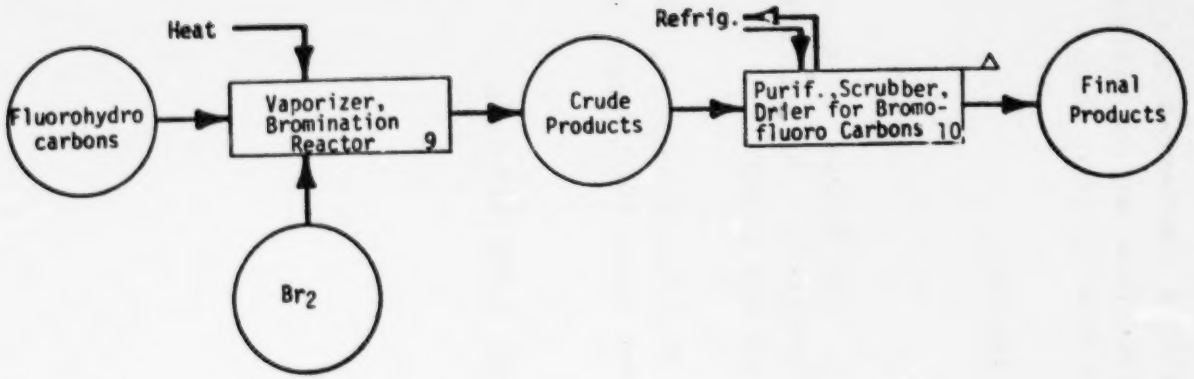

FIGURE 5. FLOWSHEET FOR THE PRODUCTION OF BROMOFLUOROCARBONS

FLUOROCARBON PRODUCTION PROCESS NUMBER 9

Bromination of Fluorohydrocarbons

1. Function

To convert fluorohydrocarbons to bromofluorocarbons. In this process $CHClF_2$ (FC-22) is converted into $CBrClF_2$; CHF_3 (FC-23) is converted into $CBrF_3$; and CH_2F_2 (FC-32) is converted into CBr_2F_2. The process is accomplished in a pyrex glass reactor through mixing and vaporizing the feed and reacting the fluorohydrocarbons with the bromine vapor. Monel or nickel tube reactors can be used in place of glass.

2. Input Materials

The fluorohydrocarbon is mixed with bromine vapors at a ratio of from 25 to 45 percent by weight of the former to 75 to 55 percent by weight of the latter. Depending upon the conditions, it is possible to prepare several different products. If the main product desired is $CBrClF_2$, a conversion of about 55% is achievable. Thus, from 150 kg. of $CHClF_2$, 82 kg. of $CBrClF_2$ is prepared.

3. Operating Parameters

The temperatures at which the reaction is performed may vary from 300 to 900°C. Normal operation is performed from 650° to 750°C. Atmospheric pressure is used.

4. Utilities

Approximately 100 kcal. of heat are required per kg. of product.

5. Waste Streams

There should be no waste streams in this process other than those occurring abnormally due to leaks or spills.

6. EPA Source Classification Code

None established.

7. References

Barnhart, W. S., U.S. Patent 2,731,505 (1956).

Purification of Bromofluorocarbons

1. **Function**

The crude products from the bromination of the fluorohydrocarbons (see process No. 9) are purified by scrubbing out the by-product hydrogen bromide (HBr) and any unreacted bromine. The scrubbed products, along with any unreacted starting material, are subsequently dried with a desiccant.

2. **Input Materials**

Into this process are fed the following materials together with their estimated quantities (per kg. of feed).

HBr	0.27 kg.
Br_2	0.006
$CBrClF_2$	0.55
CBr_2F_2	0.06
$CHClF_2$	0.12
HCl	0.004

The feed is scrubbed with water (or aqueous caustic) to remove the HBr and trace quantities of Br_2 and HCl. The bromofluorocarbons and starting material are passed through a desiccant (silica gel, molecular sieves, etc.) and the dried products recovered. These may be used as a mixture or separated by distillation, if necessary.

3. **Operating Parameters**

The gases are scrubbed with ambient temperature water and dried at atmospheric pressure. The dried gases are cooled to about - 5°C, liquefied, and stored.

4. Utilities

For a production plant having a capacity of 200 kg. per day, it is estimated that 0.5 kg. of scrubbing water is required and approximately 60 kcal. of heat need to be withdrawn from the system per kg. of product.

5. Waste Streams

Since the aqueous HBr is too valuable to be discarded, it is usually recycled to recover the bromine values or diverted to other plant uses. Traces of HBr, HCl, and bromofluorocarbons may escape due to pump leaks, etc., but in general no major quantity of the products is lost to air, water, or ground.

6. EPA Source Classification Code

None established.

7. References

Barnhart, W. S., U.S. Patent 2,731,505 (1956).

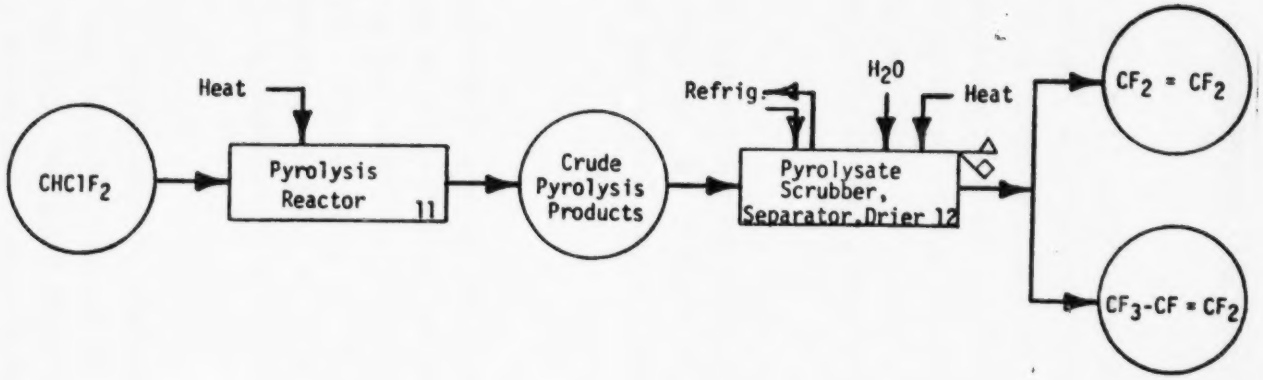

FIGURE 6. FLOWSHEET FOR THE PYROLYSIS OF CHLORODIFLUOROMETHANE (FC-22)

Pyrolysis of Chlorodifluoromethane

1. Function

To prepare tetrafluoroethylene ($CF_2= CF_2$) and hexafluoropropylene (CF_3-CF=CF_2) from chlorodifluoromethane ($CHClF_2$)(FC-22). Other fluorochemicals obtained in small amounts from this process include difluoromethane (CH_2F_2), trifluoromethane (CHF_3), chlorotrifluoromethane , hexafluoroethane, octafluorocyclobutane, and trifluoroethylene. These latter fluorochemicals, as well as HCl, are by-products of the pyrolysis and are not made commercially by this route.

Several equipment designs have been employed for the above process. In general, the combustion chamber can be made of ceramic or high temperature steel, and the reaction tube may be made of sintered aluminum oxide or platinum.

2. Input Materials

Normally, chlorodifluoromethane is the feed material to this process. However, other feed materials such as tetrafluoromethane, trifluoromethane, and octafluoropropane, may also be used in this process to produce the same major products. In some reactor designs, finely divided carbon is used as a quenching medium to prevent further reaction of the tetrafluoroethylene.

3. Operating Parameters

The pyrolysis may be performed at 850-1300°C. The pyrolysis products are rapidly cooled to about 500°C to prevent further reaction. Pressures of 0.1 to 0.5 kg/cm^2 are frequently used with preferred contact times of 0.1 to 0.001 seconds. Usually the process is performed non-catalytically.

4. Utilities

Heat for this pyrolytic process may be provided by electricity or combustion gases. Electric arcs or oxyhydrogen torches have also been used. The heat or power requirements are entirely dependent upon the quantity and type of starting material fed to the process. However, it is estimated that about 20 kcal of heat per mole of chlorodifluoromethane are required.

5. Waste Streams

Other than leaks or spills, there should be no waste streams from the above process.

6. EPA Source Classification Code

None established.

7. References

1) Okamura, K., et al, U.S. Patent 3,221,070 (1965).
2) Benning, A. F., et al, U.S. Patent 2,406,794 (1946).
3) Dennison, J. T. et al, U.S. Patent 2,852,574 (1958).
4) Scherer, O., et al, U.S. Patent 2,994,723 (1961).
5) Farlow, M. W., U.S. Patent 2,709,182 (1955).
6) Downing, F. B., et al, U.S. Patent 2,551,573 (1951).

Pyrolysate Scrubber, Separator, Drier

1. Function

To separate into pure components the pyrolysate from chlorodifluoromethane (FC-22). The two major products, tetrafluoroethylene ($CF_2=CF_2$) and hexafluoropropylene ($CF_3-CF=CF_2$) must be highly pure before these monomers can be satisfactorily homo- or copolymerized. Separation and purification is usually accomplished by a series of scrubbing, distillation, adsorption and desorption steps under super-atmospheric pressures. Stainless steel equipment is adequate for this process.

2. Input Materials

The feed into this process consists of all the products of the pyrolysis from process 11. These usually consist of tetrafluoroethylene, hexafluoropropylene, hydrogen chloride, and the unreacted starting material, chlorodifluoromethane. The following may also be present in minor amounts: trifluoromethane, chlorotrifluoromethane, hexafluoroethane, difluoromethane, dichlorodifluoromethane, and octafluorocyclobutane. The conversion of chlorodifluoromethane into tetrafluoroethylene is dependent upon the pressure under which pyrolysis occurs. Normally, the pressure is kept at about 0.40 kg/cm^2, whereupon the conversion is about 30% and the yield of tetrafluoroethylene is about 90%. Therefore the materials fed to this process based on the kg of product obtained, are approximately

chlorodifluoromethane	3.5 kg.
tetrafluoroethylene	1.0 kg.
hexafluoropropylene	0.03 kg.
hydrogen chloride	0.7 kg.
minor products	0.02 kg.

3. Operating Parameters

Pressure: 0.3-16 kg/cm^2

Temperature: -20° to 0°C

The mixture of products obtained is extremely difficult to separate by distillation. Cold methanol dissolves all the products except the tetrafluoroethylene and hexafluoropropylene. The dissolved materials are later stripped from the methanol and recycled or packaged.

4. Utilities

It is estimated that electrical power for compressors and refrigeration amounts to 5 kWh/kg of product. Heat input (steam) for distillation processes is estimated to be about 500 kcal/kg. Water consumption is estimated to be about 500 ℓ./kg of product.

5. Waste Streams

Small quantities of tar may be formed in the process which are discarded (ground burial). Due to the process pressures involved, fluorocarbon vapor leaks may occur occasionally. The aqueous hydrochloric acid resulting from the scrubbing of the product may be transferred to other plant uses. Drying agents (desiccants) may be regenerated or discarded.

6. EPA Source Classification Code

None established.

7. References

Okamura, K., et al, U.S. Patent 3,221,070

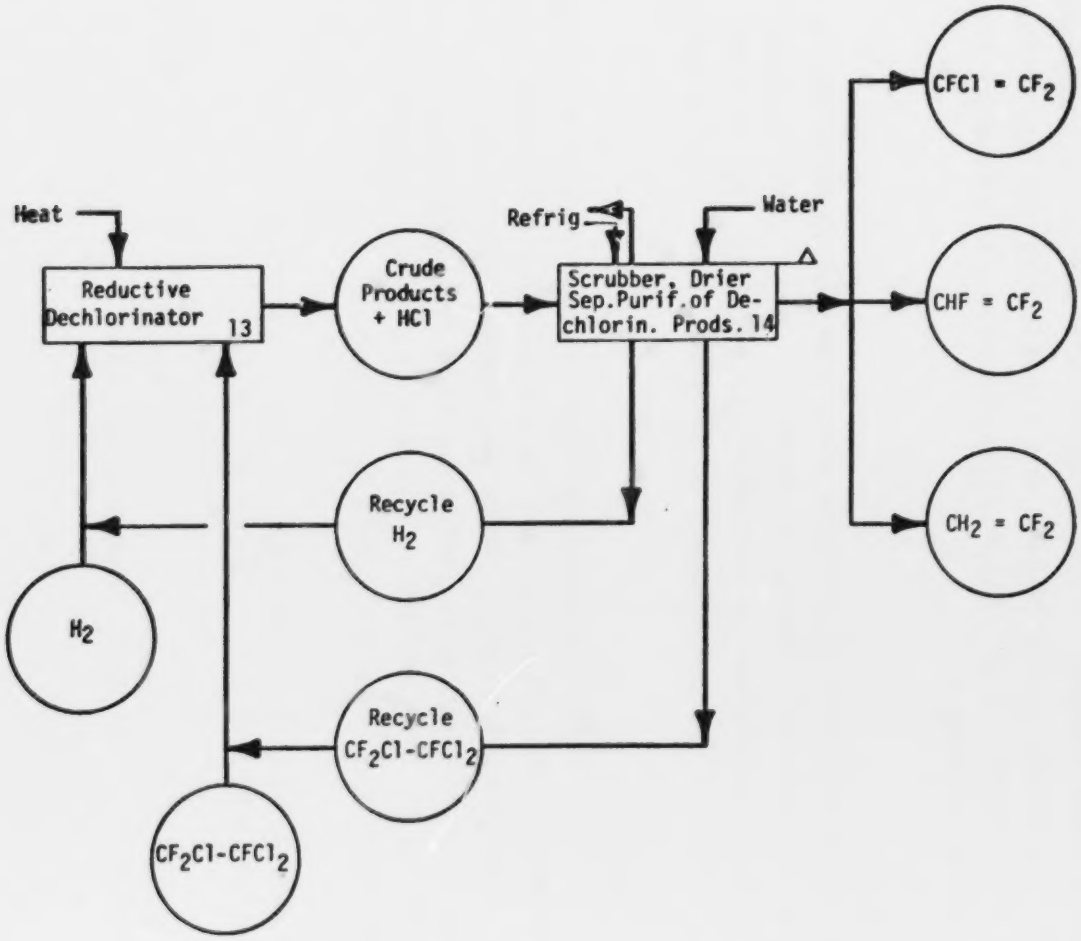

FIGURE 7. FLOWSHEET FOR THE REDUCTIVE DECHLORINATION OF 1,1,2-TRICHLOROTRIFLUOROETHANE

Reductive Dechlorination of 1,1,2-Trichlorotrifluoroethane

1. Function

To prepare chlorotrifluoroethylene by reductive dechlorination of 1,1,2-trichlorotrifluoroethane (FC-113), according to the following reaction:

$$CF_2Cl\text{-}CFCl_2 \xrightarrow{H_2} CF_2{=}CFCl + 2HCl.$$

The vapor phase reaction is usually carried out at elevated temperatures in the presence of hydrogen and a catalyst. In addition to the desired product, two by-products predominate. The products are later separated in a separate process (see process No. 14). The reaction may also be conducted using zinc in ethanol, according to :

$$CCL_2F\text{-}CClF_2 \xrightarrow[EtOH]{Zn} CClF{=}CF_2 + ZnCl_2$$

2. Input Materials

Based on 1 mole of product, the following feed rates are used:
1,1,2-trichlorotrifluoroethane - 1.3 moles/min.
Hydrogen gas - 2.3 moles/min.

3. **Operating Parameters**

Temperature:	**490 - 580°C**
Pressure:	**1.05 kg/cm²**
Flow rate:	**1,1,2-Trichlorotrifluoroethane - 15 moles/min. Hydrogen - 3 moles/min.**
Reactor size:	**50 liters**
Catalyst:	**Copper gauze, copper-cobalt on MgO, or MgF**

4. **Utilities**

It is estimated that 15 kcal/mole of heat are required to carry out this reaction. The energy may be supplied as gas or electricity.

5. Waste Streams

The products from the above reactor are separated in the next process. Other than leaks or spills, no waste streams should be emitted from this closed system process. In the case of reaction with zinc in ethanol, the $ZnCl_2$ formed may present a disposal problem.

6. EPA Source Classification Code

None established.

7. References

Mantell, R. M., U.S. Patent 2,697,124 (1954).

Separation and Purification of Products from Dechlorination of 1,1,2-Trichlorotrifluoroethane

1. Function

To separate chlorotrifluoroethylene, trifluoroethylene, vinylidene fluoride and hydrogen chloride and purify the monomers. A mixture of these materials along with the unreacted starting material from the reductive dechlorination step (see process 13) are fed into this process. The main product, chlorotrifluoroethylene, is later used in homo- and copolymerizations. The two by-products, trifluoroethylene and vinylidene fluoride, are not made commercially by this process. (See processes 20 and 23). These materials are separated by fractional distillation and the HCl is usually scrubbed out with water. Stainless stell materials may be used.

2. Input Materials

The feed to this process is the same as the product from the dechlorination process (see process 13), and consists of chlorotrifluoroethylene, trifluoroethylene, vinylidene fluoride and HCl, along with the unreacted 1,1,2-trichlorotrifluoroethane and hydrogen.

3. Operating Parameters

Temperature:	0 to -20°C
Pressure:	140 kg/cm^2
Flow rate:	approximately 15 moles/min.

4. Utilities

It is estimated that 15 kcal/mole of heat need to be withdrawn from the system by refrigeration. Additionally, it is estimated that 5 kWh of electricity are required for compression of the gases. About 0.25 ℓ. of water per mole of product is needed for scrubbing.

5. Waste Streams

For every mole of product, about 2 moles of HCl are formed. When dissolved in water, this aqueous acid can be transferred to other plant uses.

6. EPA Source Classification Code

3-01-011-02 BYPRODUCT W/SCRUB

7. References

Mantell, R. M., U.S. Patent 2,697,124 (1954).

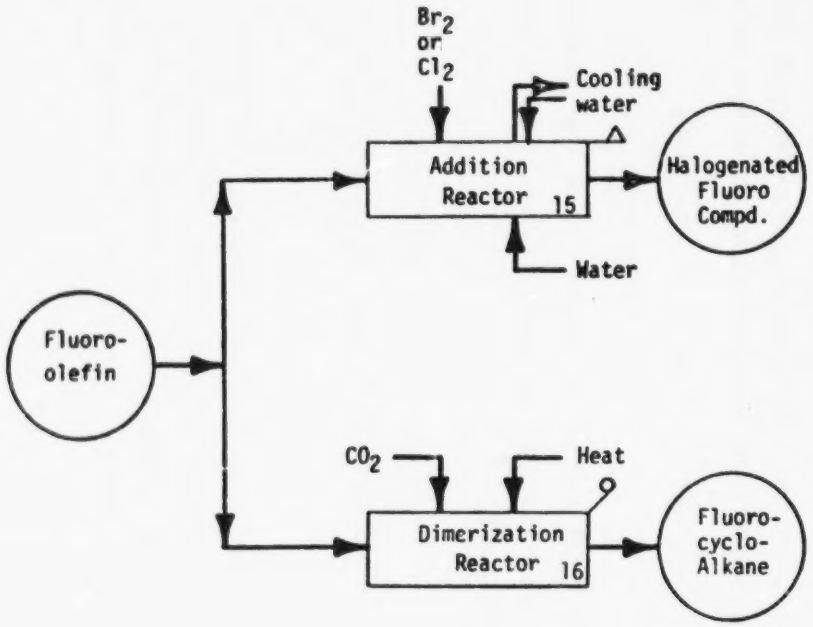

FIGURE 8. FLOWSHEET FOR THE REACTIONS OF FLUOROOLEFINS

Addition of Halogens to Perfluoroalkenes

1. Function

To prepare brominated and chlorinated fluorocarbons by the chemical addition of bromine or chlorine to a perfluoroolefin. These exothermic reactions may be performed in the vapor phase or, alternatively, may be performed by bubbling the olefin into the liquid halogen. The equation for the reaction is shown below.

$$R\text{-}CF{=}CF_2 + X_2 \longrightarrow R\text{-}\underset{X}{CF}\text{-}\underset{X}{CF_2}$$

where X=Br,Cl.

The reaction proceeds quite cleanly - with the formation of only the product and with little or no by-products. A glass or monel reactor is satisfactory.

2. Input Materials

A halogen and a perfluoroolefin are the only feed materials.

3. Operating Parameters

If the perfluoroolefin is bubbled through the liquid halogen, the halogen must be cooled with water. The reaction normally occurs at atmospheric pressure. No catalyst is required. If reacted in the vapor phase, the product is passed through a cooling condenser.

4. Utilities

Only cooling water is required. The amount of cooling is dependent upon the rate of input. It is estimated to be from 160 to 240 kcal/kg. of product, depending upon which product is made.

5. Waste Streams

Traces of halogen gases may leave the reactor as an effluent. These may be scrubbed with water, which is sent to a waste disposal pond.

6. EPA Source Classification Code

None established.

7. References

1) Ruff, O., and Bretschneider, O., Chem. Abstr. 27, 2131 (1933).

2) Lacher, J. R., et al., J. Amer. Chem. Soc., 71, 1330 (1949).

3) Patrick, C. R., "Advances in Fluorine Chemistry," Vol. 2, Stacey, M., Tatlow, J. C., and Sharpe, A. G., Editors, Butterworths, Washington, DC, 1961

Dimerization of Fluoroolefins

1. Function

To prepare cyclic perfluoroalkanes by homodimerization of a perfluoroalkene. Tetrafluoroethylene is converted into perfluorocyclobutane. This is an alternative process for the preparation of perfluorocyclobutane (see process 11). This reaction is amenable to homo- and codimerizations of other olefins as well.

2. Input Materials

For the preparation of octafluorocyclobutane, the material introduced in this process is tetrafluoroethylene along with an inhibitor such as CO_2 (3).

3. Operating Parameters

The temperature is maintained at 150-200°C and the pressure is usually 14-18 kg/cm^2. Under normal operating conditions, the cyclic dimer is formed, with the unreacted monomer tetrafluoroethylene being recycled.

4. Utilities

It is estimated that approximately 2 kWh of electrical energy are required for compressors. Approximately 10 kcal/kg of heat energy are required.

5. Waste Streams

Other than leaks or spills, a small quantity of CO_2 and fluorocarbons may be lost in this pressurized closed cycle process.

6. EPA Source Classification Code

None established.

7. References

1) Banks, R. E., "Fluorocarbons and Their Derivatives," University Chemistry Series, MacDonald Technical and Scientific, London, 1970, pp 7-69.

2) Wüst, H. A., U.S. Patent 3,101,304 (1963).

3) Knunyants, I. L., et al. USSR Patent 173,733 (1965).

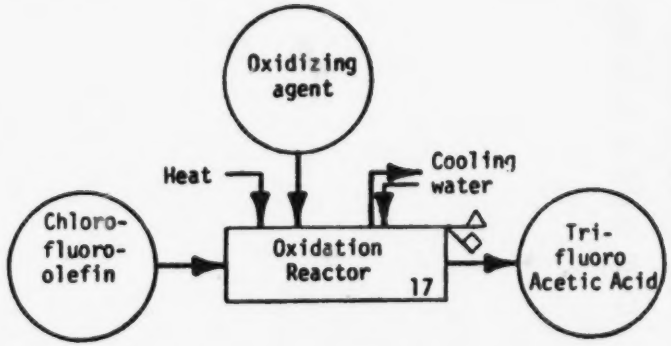

FIGURE 9. FLOWSHEET FOR THE OXIDATION OF CHLOROFLUOROOLEFINS

Oxidation of Chlorofluoroolefins

1. Function

To prepare trifluoroacetic acid via oxidation of a double bond in olefins. This chemical reaction is a laboratory scale alternative to the commercial electrochemical process for making trifluoroacetic acid. The product of oxidation may be extracted and distilled, or the aqueous alkaline solution may be evaporated to dryness, then acidified, to recover the desired product. Trifluoroacetic acid may also be prepared from 1,1,2-trichlorotrifluoroethane (FC-113) by forming the isomer CF_3CCl_2 which is then hydrolyzed to CF_3COCl by fuming sulfuric acid and then further hydrolyzed to the acid by water.

2. Input Materials

An alkaline oxidizing agent is usually used for the chemical oxidation. Frequently potassium permanganate along with a small amount of sodium or potassium hydroxide are used. Potassium dichromate has also been used. The fluoroolefin compound most frequently used is:

$$CF_3-\underset{Cl}{C}=\underset{Cl}{C}-CF_3$$

although the octafluorobutene-2 has also been used. The yields of trifluoroacetic acid are about 80-85% based on the moles of trifluoromethyl compound fed. About two moles of $KMnO_4$ are required per mole of product.

3. Operating Parameters

Normally the organic olefin is added portionwise to the oxidizing agent in this batch process, but the reverse is also effective.

The solution is maintained at 80-100°C during the oxidation which occurs at atmospheric pressure. The feed rate is dependent upon the rate of oxidation; normally from 1-10 moles/day are added.

4. Utilities

It is estimated that 30 kcal of heat are needed per mole of product formed. About 500 ℓ of cooling water are required per mole of product.

5. Waste Streams

The by-product, manganese dioxide (MnO_2), can be recovered or sent to ground burial. Aqueous potassium chloride may be sent to a disposal pond. Waste from the acid hydrolysis of CF_3CCl_3 would be mainly spent sulfuric acid, which could be neutralized and sent to pond or sewer.

6. EPA Source Classification Code

None established.

7. References

1) Babcock, J. H., and Kischitz, A. D., U.S. Patent 2,414,706 (1947).

2) McBee, E. T., Wiseman, P. A., and Bachman, G. B., Ind. Eng. Chem., 39, 415 (1947).

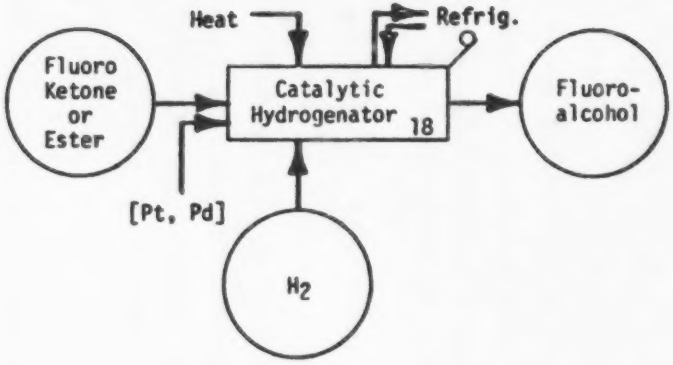

FIGURE 10. FLOWSHEET FOR THE PRODUCTION OF FLUOROALCOHOLS BY CATALYTIC HYDROGENATION

Production of Fluoroalcohols by Catalytic Hydrogenation

1. Function

To prepare fluorinated alcohols by the catalytic reduction of ketones or fluorinated esters, according to following general reaction:

$$R\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CF_2)_nF + 2H_2 \xrightarrow{\text{cat.}} ROH + HOCH_2\text{-}(CF_2)_nF$$

The pure fluorinated alcohol may be recovered by distillation. The reduction is frequently carried out in a steel bomb. This process finds use in the preparation of hexafluoro-2-propanol, but, because of the relatively low yield, it is not normally used for preparation of 2,2,2-trifluoroethanol.

2. Input Materials

In addition to the ketone or ester and hydrogen gas, a catalyst is required. The composition of the catalyst may involve palladium, or platinum impregnated on alumina (1), or it may involve a copper-chromium compound (2). Conversions and yields vary with the pressure, temperature, catalyst, and compound used.

3. Operating Parameters

If the process is carried out in a pressure vessel (bomb), high pressure (350-700 kg/cm^2) is required. If carried out under low pressure (<5 kg/cm^2), conversions usually are lower. Temperatures may vary from 50-300°C. The amount of catalyst may vary from 0.5-300% based on the weight of the ketone or ester. In one example, 100 cm^3 of Ru-Al_2O_3 catalyst (0.5% Ru) was charged into a 1.5 cm internal diameter fused alumina reactor 91 cm long which was heated over 76 cm of length in an electric furnace. The internal temperature was maintained at 265°C and a mixture of 183 g of 2,2,2-trifluoroethyl trifluoroacetate and 46 ℓ. of hydrogen was passed through the reactor in a 5 hour period. The residence time was approximately 15 seconds. The exit gases

were cooled in a dry ice-trap and the condensate was later fractionated into 45 g. of starting material and 40 g. of 2,2,2-trifluoroethanol representing a 21% conversion. The yield for the conversion of hexafluoroacetone to hexafluoro-2-propanol is >90%.

4. Utilities

It is estimated that about 20 kcal of heat are required per mole (100 g.) of product formed. Electrical heating is usually used. Water (100 kg/kg) or refrigeration is required for condensation of the product.

5. Waste Streams

Excess hydrogen can be vented to the atmosphere. The catalyst will need replacement after a period of time due to handling losses. It is estimated that this will involve not more than 1 g./kg of product.

6. EPA Source Classification Code

None assigned.

7. References

1) Anello, L. G., and Cunningham, W. J., U.S. Patent 3,356,746 (1967).

2) Case, L. C., and Yan, T-Y, U.S. Patent 3,314,987 (1967).

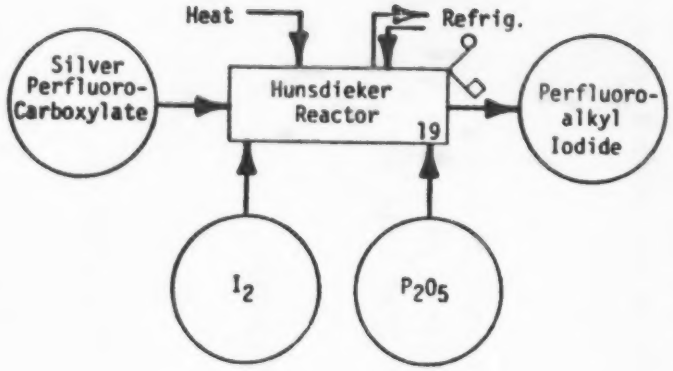

FIGURE 11. FLOWSHEET FOR THE PRODUCTION OF PERFLUOROALKYL IODIDES

Preparation of Perfluoroalkyl Iodides

1. Function

To convert perfluorocarboxylic acids to perfluoroalkyl iodides. The batch reaction involves careful heating of the dry silver salt of a perfluorocarboxylic acid with iodine vapors according to the following general equation:

$$R_f\text{-}COOAg + I_2 \longrightarrow R_fI + CO_2 + AgI$$

Any mono- or difunctional perfluorocarboxylic acid can be converted in this manner, including trifluoroacetic and perfluoroheptanoic acids. This Hunsdieker reaction is usually carried out in glass equipment on a small scale; steel should also be satisfactory.

2. Input Materials

Assuming a typical average yield of 90% of the perfluoroalkyl iodide from the perfluorocarboxylic acid, input materials (per mole of product) consist of:

1.11 moles silver perfluorocarboxylate
1.44 moles of iodine (30% excess)
0.10-0.20 moles phosphorus pentoxide (desiccant)

3. Operating Parameters

The reaction is carried out at atmospheric pressure and at 100-160°C. A 3-ℓ. flask with adequate air and water-cooled condensers is adequate to prepare one mole of the perfluoroalkyl iodide.

4. Utilities

It is estimated that about 2 kcal/mole of heat is required, usually electrical energy, to carry out this process. About

100 *l.* of cooling water per mole of product is needed. An additional 5 kcal/mole of heat needs to be withdrawn from the product prior to packaging.

5. Waste Streams

A small amount of phosphoric acid (or anhydride) will be discharged from this process; the quantity depends upon the dryness of the feed. This can be sent to a waste pond. One mole of silver iodide is formed per mole of product. This is recovered and recycled after appropriate treatment. Carbon dioxide (1 mole/mole) is also evolved in the process.

6. EPA Source Classification Code

None established.

7. References

1) Hudlicky, M., "Chemistry of Organic Fluorine Compounds," The Macmillan Co., New York, 1962.

2) Crawford, G. H., and Simons, J. H., J. Amer. Chem. Soc., 75, 5737 (1953).

3) Banks, R. E., "Fluorocarbons and their Derivatives," Second Edition, MacDonald Technical and Scientific, London, 1970.

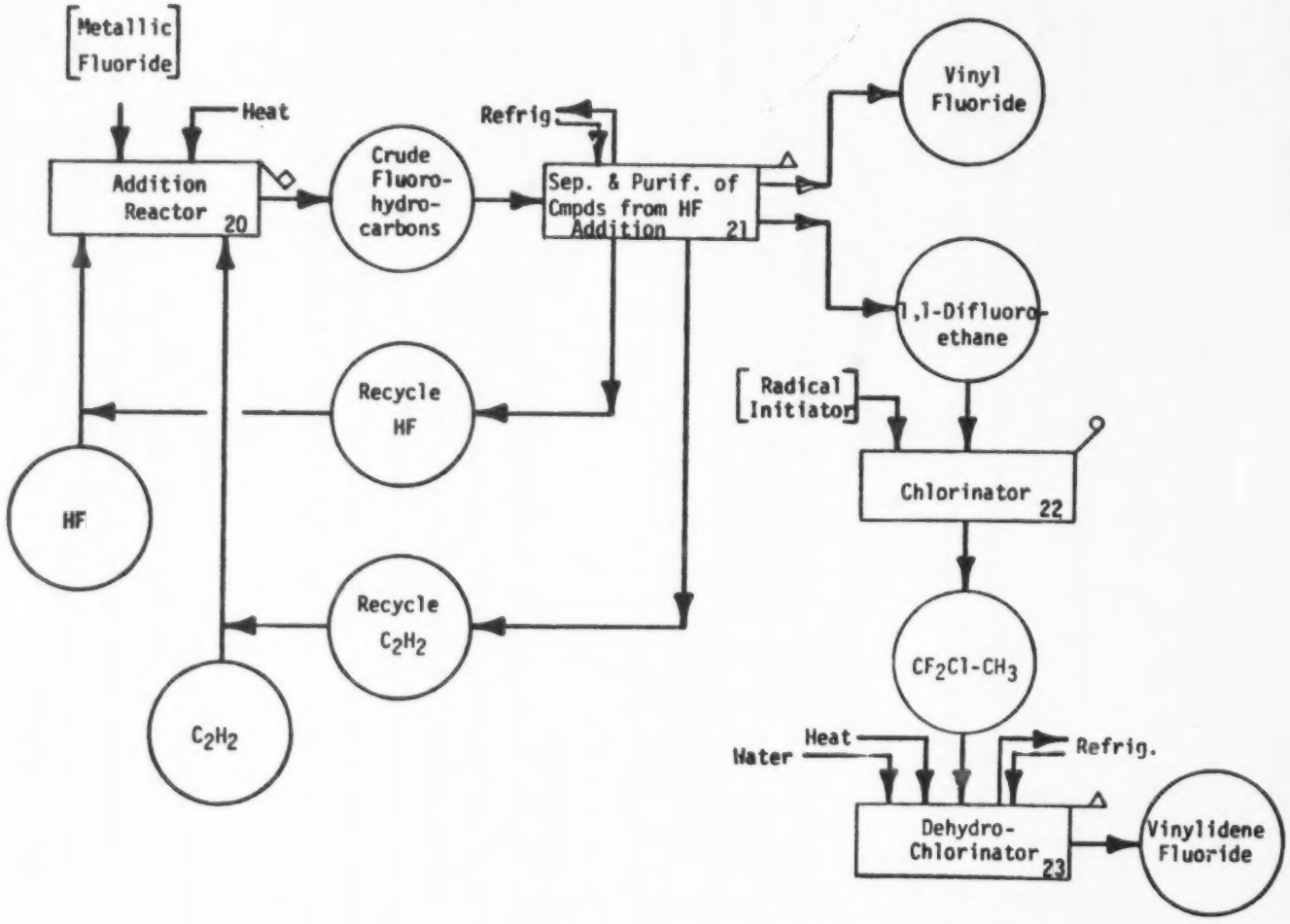

FIGURE 12. FLOWSHEET FOR THE PRODUCTION OF FLUOROCARBONS FROM ACETYLENE

HF Addition to Acetylene

1. Function

To convert unsaturated hydrocarbons into fluorohydrocarbons by the chemical addition of HF. In this process, with the addition of HF, acetylene is converted to vinyl fluoride which is then further reacted to 1,1-difluoroethane according to the following reaction:

$$CH{\equiv}CH + HF \rightarrow CH_2{=}CHF + HF \rightarrow CH_3CHF_2$$

The hydrofluorination reaction is usually carried out in a vertical tubular reactor with HF and HC≡CH feed inlets at the base and product outlet at the top. The tube is filled with a powdered catalyst. The reactor may be made of stainless steel, Monel, or high nickel alloys.

2. Input Materials

A mole ratio of hydrogen fluoride to acetylene of between one and five is usually used, and the reaction is carried out in the vapor phase. Approximately one volume of powdered catalyst is required per 100 volumes per minute of gas passing through the reactor. About half of the product is vinyl fluoride and the other half is mainly 1,1-difluoroethane (based on acetylene).

3. Operating Parameters

The vaporized feed is fed into the reactor at from 10 to 4000 ml. of acetylene per gram of catalyst per hour. Preferably the feed rate is approximately 100 volumes/volume of catalyst per hour. Several catalysts are capable of speeding up the reaction--these are usually metal fluorides, e.g., aluminum fluoride. The catalyst is normally impregnated powdered alumina. The feed rate is highly dependent upon the activ-

ity of the catalyst. The reaction is normally carried out at a temperature of 250 to 400°C and at a pressure of one atmosphere or higher. It is estimated that a reactor 10 x 50 cm will produce about 200 g of product/hr.

4. Utilities

Assuming a production rate of 200 g of product/hr., about 20 kcal. of heat energy are needed to heat the reactor. This is usually accomplished either by electric heaters or molten salt baths.

5. Waste Streams

The products from the reactor consisting of vinyl fluoride, 1,1-difluoroethane, and HF, along with small quantities of acetylene, are sent to the next process (process 21) for separation. Depending upon the conditions under which this process is operated, the lifetime and activity of the catalyst is such that replacement is eventually needed. This solid waste can be disposed of by burial. The only other waste which should occur is due to leaks and spills.

6. EPA Source Classification Code

None established.

7. References

1) Christoph, F. J., et al., U.S. Patent 3,178,484 (1965).

2) Petit, R., et al., U.S. Patent 3,187,060 (1965).

3) Clark, J. W., U.S. Patent 2,626,963 (1953).

4) Swamer, F. W., U.S. Patent 2,830,101 (1958).

Separation and Purification of Fluorohydrocarbons from HF Addition

1. Function

To separate the crude products and starting materials from the HF-addition process. In this process, vinyl fluoride, 1,1-difluoroethane and small quantities of the starting materials, acetylene and hydrogen fluoride, are separated by distillation under pressures higher than atmospheric. Materials of construction will be Monel or nickel-clad steel.

2. Input Materials

An estimated 30% of the material entering this process is vinyl fluoride, another 35% is 1,1-difluoroethane, the remainder being hydrogen fluoride (30%) and acetylene (2%).

3. Operating Parameters

The operation of this process is usually closely integrated with the preceding process, and flow rates will be dependent upon the rate of production from process 20.

The gaseous materials entering this process are cooled and compressed. After cooling to about 0°C under pressures of up to 20 kg/cm^2, the products are separated by distillation.

The desired products may be passed through a scrubber and drier, if necessary, before being sent to storage. The hydrogen fluoride and acetylene are recycled as feed to the HF-addition process (process 20).

4. Utilities

At a production rate of 200 g of product/hr., about 75 kcal/kg

of heat need to be withdrawn from the system. The compressor will require approximately 5 kWh/kg of product.

5. Waste Streams

Small quantities of fluorohydrocarbons may be lost due to leaks and spills. If the vinyl fluoride is scrubbed with 5% caustic (NaOH), small quantities of aqueous NaF may be sent to waste water. The quantity of NaF formed is highly dependent upon the efficiency of the process at a particular location.

6. EPA Source Classification Code

None established.

7. References

1) Houben-Weyl "Methoden der Organischen Chemie", Vol. 5, Part 3, Georg Thieme Verlag, Stuttgart, 1962, pp 8-14.

2) Air Reduction Co., Inc., British Patent 790,824 (1958).

Chlorination of 1,1-Difluoroethane

1. Function

To convert 1,1-difluoroethane into 1-chloro-1,1-difluoroethane according to the following reaction:

$$CHF_2\text{-}CH_3 + Cl_2 \longrightarrow CClF_2\text{-}CH_3 + HCl$$

The reaction may be performed in a stainless steel, nickel, or Monel reactor, usually tubular.

2. Input Materials

The feed materials are 1,1-difluoroethane and chlorine usually two moles of the former to about one of the latter. This is arranged to ensure complete reaction of the chlorine. A free-radical initiator (usually 0.1-0.2% by weight, based on the amount of difluoroethane) is added in the feed. The HCl gas evolved may be forwarded to other plant uses or may be scrubbed out with water or aqueous sodium hydroxide.

3. Operating Parameters

The mixture of difluoroethane, chlorine and catalyst is pre-heated to 75-100°C, at which time free radical initiation begins. An exothermic reaction ensues and the rate of feed is such that the subsequent reaction temperature is maintained between 150 and 200°C. Pressures of about 27-33 kg/cm^2 are normally used. The preferred residence time is from 2 to 8 seconds. The catalyst normally used is azo-bis-isobutyronitrile; however, any catalyst capable of forming free radicals above room temperature should function as an initiator.

4. Utilities

Although the chlorination reactor can be cooled externally by

water, it normally is not. No other utilities are usually involved.

5. Waste Streams

If aqueous caustic is used to scrub the HCl by-product, the waste stream will consist of aqueous NaCl. If the gaseous by-product is desired in other plant uses, it can be transferred as such.

6. EPA Source Classification Code

None established

7. References

Wolf, H. O., U.S. Patent 3,047,642 (1962).

Dehydrochlorination of 1-Chloro-1,1-Difluoroethane

1. Function

To prepare vinylidene fluoride ($CF_2=CH_2$) by the pyrolytic removal of hydrogen chloride from 1-chloro-1,1-difluoroethane according to the following reaction.

$$CClF_2\text{-}CH_3 \longrightarrow CF_2=CH_2 + HCl$$

This vapor phase reaction is usually carried out, in the absence of a catalyst, in a stainless steel or nickel heated tube.

2. Input Materials

Normally, 1-chloro-1,1-difluoroethane is the only feed material to this process. The process gives high conversions and essentially quantitative yields, i.e., one mole of feed produces one mole of product. Water, or aqueous caustic (NaOH) may be used to scrub out the hydrogen chloride eliminated during the reaction. This requires 1 mole of NaOH per mole of product.

3. Operating Parameters

The optimum temperatures for dehydrohalogenation are 700-850°C. The reaction is normally performed at atmospheric pressure or slightly lower, with reaction times of less than 1 second and at space velocities of 100 to 500 per hour.

4. Utilities

This endothermic reaction requires about 20 kcal/mole of feed. The reactor tube can be heated with gas or electricity. If water is used to scrub the products, 1 liter of water is required for every 10 moles of product. Compression and refrigeration are needed to package the vinylidene fluoride. An

estimated 1 kWh/mole is required.

5. Waste Streams

If water is used for scrubbing, the aqueous (35%) hydrochloric acid can be transferred to other plant uses. If 10% aqueous caustic is used, the aqueous salt (NaCl) solution could be disposed of in a waste pond. One liter of salt solution will be formed for every 2.5 liters of vinylidene fluoride formed.

6. EPA Source Classification Code

3-01-011-02 BYPRODUCT W/SCRUB

7. References

1) Scherer, O., et al. U.S. Patent 3,183,277 (1965).

2) Feasley, C. F., et al. U.S. Patent 2,627,529 (1953).

3) Miller, C. B., U.S. Patent 2,628,989 (1953).

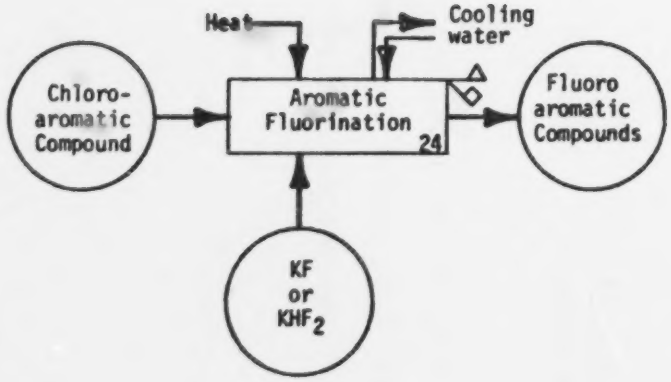

FIGURE 13. FLOWSHEET FOR THE PRODUCTION OF FLUOROAROMATIC COMPOUNDS

Production of Fluoroaromatic Compounds

1. Function

To prepare fluorine-substituted benzenes, pyridines, pyrimidines, etc., by the action of a metal fluoride on the corresponding chlorine-substituted benzene, etc. This rather recently developed process is being used to make limited amounts of the fluoroaromatic compounds. Certain fluoroaromatics can be made in glass equipment in a solvent; others are more commonly made neat (without solvent) in pressurized stainless steel or Monel vessels. Aromatic fluorine compounds have historically been prepared by diazotization of amines in HF alone or with complexing agents such as BF_3 to form diazonium salts which decompose to aromatic fluorine compounds.

2. Input Materials

The following are typical of input materials together with products obtained in this batch process.

Table 4. TYPICAL FLUOROAROMATIC COMPOUNDS AND INPUT MATERIALS

Feed Material	Product (% yield)
2-Chloropyridine	2-Fluoropyridine (74)
2,6-Dichloropyridine	2,6-Difluoropyridine (80)
2,4,6-Trichloropyrimidine	2,4,6-Trifluoropyrimidine (90) +Chlorodifluoropyrimidine (9) +Dichlorofluoropyrimidine (0.9)
Nitrobenzene	3-Fluoronitrobenzene +2-Fluoronitrobenzene +4-Fluoronitrobenzene
1,3,5-Trichlorobenzene	3,5-Dichlorofluorobenzene (54.5) 3,5-Difluorochlorobenzene (47.7) 1,3,5-Trifluorobenzene (56.2)

CsF or KF may be used as the fluorinating agent depending upon the substrate being fluorinated. Usually an 8-10% excess of the fluorinating agent is used.

3. Operating Parameters

When the process is performed in a solvent, the reaction is carried out at about 100-200°C at atmospheric pressure. When performed neat, the temperatures are about 300-400°C and the pressures 20-25 kg/cm^2.

4. Utilities

It is estimated that the heat required per mole of product is 10 kcal. This may be in the form of electrical or gas heat. About 100 ℓ. of cooling water will be required per mole of product.

5. Waste Streams

For each mole of chlorine atoms replaced, there will be one mole of KCl formed. This can be discharged to a waste pond. The solvent, when used, can be recycled or discharged to a waste pond.

6. EPA Source Classification Code

None assigned.

7. References

1) Boudakian, M. M., J. Hetero. Chem., 5, 683 (1968).

2) Boudakian, M. M., U.S. Patent 3,296,269 (1967).

3) Boudakian, M. M., U.S. Patent 3,280,124 (1966).

4) Boudakian, M. M., and Kaufman, C. W., U.S. Patent 3,314,955 (1967)

5) Shiley, R. H., Dickerson, D. R., and Finger, G. C., J. Fluorine Chem., 2, 19 (1972); 1, 415 (1971); 4, 111 (1974); 3, 113 (1973).

6) Pavlath, A.E. and Leffler, A.L., "Aromatic Fluorine Compounds", ACS monograph No. 155, Reinhold, New York, 1962.

HF PRODUCTION PROCESSES

Hydrogen fluoride, important as the principal fluorinating agent, is obtained by treating acid grade fluorspar (CaF_2) with sulfuric acid. The impure fluorspar is mined and beneficiated to obtain material of adequate purity for use in producing fluorocarbons. Process flowsheets and process descriptions for this segment of the industry follow. Table 5 lists the processes involved in the production of HF.

Table 5. PROCESSES FOR HF PRODUCTION

25.	Mining of Fluorspar
26.	Fluorspar Beneficiation
27.	Agglomeration of Fluorspar
28.	Hydrogen Fluoride Generation
29.	Hydrogen Fluoride Purification

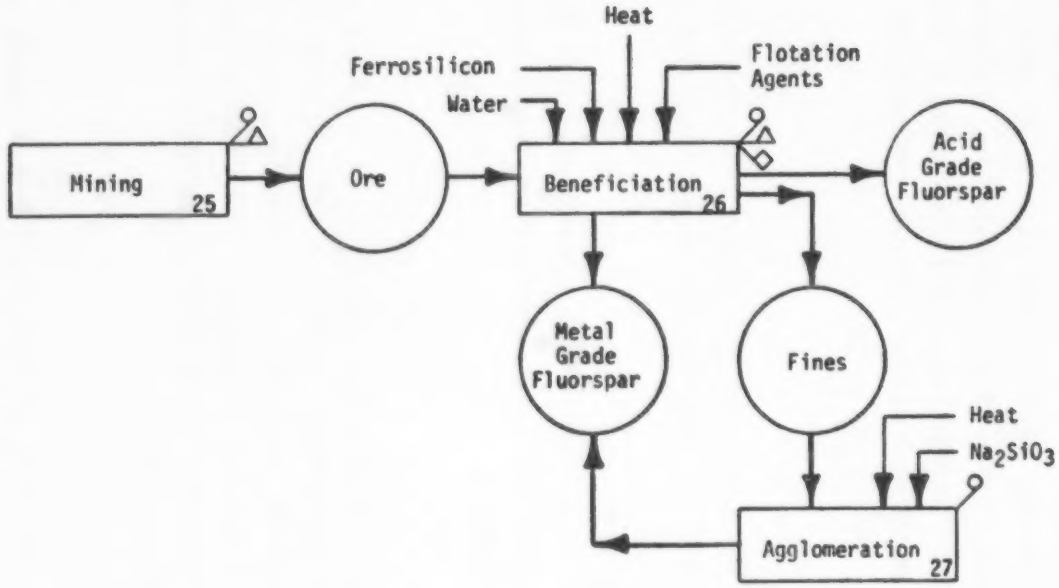

FIGURE 14. FLOWSHEET FOR THE PRODUCTION OF FLUORSPAR

Mining of Fluorspar

1. Function

To obtain the mineral from the solid ore deposits found in beds or veins in the earth. The mining is done by metal mining practices, usually by top-slicing, cut-and-fill, and shrinkage and open stoppage. Bedded deposits are usually worked by the room-and-pillar system. Mining is done by shafts, drifts, and open cuts.

2. Input Materials

Essentially none are required other than the utilities and services required to support the personnel and equipment.

3. Operating Parameters

Mines range in size from small operations with mostly hand operated equipment to large operations using extensively mechanized equipment.

4. Utilities

Large quantities of air are required to support personnel and mechanized equipment. Small quantities of electricity are used for motors, lights, etc., but no large quantities are required in mining fluorspar. Amounts of water used will vary considerably from mine to mine, depending upon the operations involved.

5. Waste Streams

Airborne fugitive dust of the same composition as the ore being mined is emitted in mining. Water from subsurface mining operations is usually contaminated with finely crushed rock as well as with oil, hydraulic fluid, gasoline, and other materials commonly used in underground operations.

6. EPA Source Classification

None established.

7. Bibliography

1) Kirk-Othmer, Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., New York, 1966.

2) Malhotra, Ramesh, Illinois Minerals Note 58, Illinois State Geological Survey, Urbana, Illinois, Oct. 1974.

Fluorspar Beneficiation

1. Function

To remove rocks and clays from the desired ore so that the crude ore may be purified. This is usually accomplished by one or more of the following procedures, depending upon the purity of the mined fluorspar.

(a) Washing. The raw ore is subjected to water sprays as it travels up the log pulper, to remove the associated clays.

(b) Heavy Media Separation. The ore minerals are separated from waste in a cone containing a suspension of finely ground ferrosilicon. The ratio of ferrosilicon to water is adjusted to give the suspension a specific gravity of about 2.6 at the top of the cone and about 2.9 at the bottom. Crude ore is introduced at the top of the cone. Heavy minerals, such as fluorspar and metal sulfides, and sink are recovered at the bottom of the cone. Light minerals float and are carried away with the overflow. Ferrosilicon is recovered magnetically and returned to the process.

(c) Crushing and Screening. The ore is fed through a crushing system for reduction to the desired fineness. Metallurgical grades require sizes between 0.95 and 3.8 cm. If the raw ore is of metallurgical grade, it is crushed and screened to the proper size with no previous refinement. To produce acid grade fluorspar, the crushed ore is fed to a ball mill which reduces the size to between 35 and 200 mesh.

(d) Flotation. Further purification is achieved by

treating the ore minerals in flotation units by use of agitated water baths to which are added frothing agents and flotation reagents to selectively coat the minerals. The sequence of reagents and flotation procedures varies according to the composition of the ore and preferences of the mill operator. Typical reagents are xanthates, acids, or sulfates.

(e) Filter and Drier. The "pulp" from the flotation cells usually contains from 20 to 40 percent solids. The concentration is increased to about 60% solids in a thickener and the resultant mixture filtered. The filter cake is further dried to less than 0.5 percent water in a rotary drier at about 250°C.

(f) Grinding. The fluorspar is ground to a minus 325 mesh after which it is transported to storage bins or enclosed hopper cars.

2. Input Materials

The primary feed to this process is the raw ore as mined from the ground. Water is required in washing the crude ore, in heavy media separation, and in the flotation steps. The quantity of water required will depend upon how many of these steps are used in the beneficiation process. It also will depend upon the purity of the fluorspar as mined. Small quantities of flotation agents are also required.

3. Operating Parameters

The bulk of the operations is carried out at ambient temperature and pressure. However, steam is required to keep the flotation cells at about 38°C.

4. Utilities

Small quantities of steam are required as indicated above.

Quantities of electricity are required to operate the various motors, pumps, etc. It is estimated that from 10 to 50 kWh of electrical energy is required per metric ton of product. Oil or gas fired driers are required. This is estimated to require 50,000 kcal per metric ton. An estimated 8,000 - 10,000 liters of water are required per metric ton of fluorspar.

5. Waste Streams

Aqueous effluents from washing and separation contain suspended solids which are usually sent to settling ponds. Tailings from the flotation operation contain both solids and the flotation agents. The latter materials are not necessarily toxic but cause excessive growth of algae and bacteria. Air emissions in the form of dust may occur; however, these are usually kept to a minimum since the ore is usually maintained in a wet condition. Drying and grinding of the purified ore present particle emission problems as well as aqueous and flotation agent emissions.

6. EPA Source Classification Code

None established.

7. References

1) Kirk-Othmer, Encyclopedia of Chemical Technology, New York, John Wiley & Sons, Inc., 1966.

2) West, L. and R. R. Walden, Milling Kentucky Fluorspar Tailings, Mining Engineering, 542-544, May 1954.

3) Maier, F. J. and E. Bellack, Fluorspar for Fluoridation, Journal of the American Water Works Association, January 1957.

Agglomeration of Fluorspar

1. Function

To recover fine grained flotation concentrates of metallurgical quality and to convert them into weatherproof dust-free pellets. The dry powder is mixed with a binder solution, pelletized, and dried. The pellets withstand outdoor exposure, including freezing and thawing and show less dusting than natural gravel spar when exposed to thermal shock in the steel furnace.

2. Input Materials

Feed to this process consists of metallurgical grade fluorspar fines in dry form along with a binder solution of sodium silicate and an undisclosed additive. The mass is pelletized in a 2.44-meter diameter rotating disc-type pelletizer, and the "green" pellets are fed into a long Porbeck baking oven where they are dried.

3. Operating Parameters

The "green" pellets are subjected to temperatures of 370-400°C for 20-30 minutes.

4. Utilities

An estimated 25,000 kcal of heat (oil or gas fired) per metric ton of finished metallurgical grade pellets is required. Approximately 5-10 kWh of electricity are required/metric ton.

5. Waste Streams

The main emission source in this operation is from the baking oven and consists of vapors from the binder solution.

6. EPA Source Classification

None established

7. References

1) Hall, W. E., and Heyl, A. V., Economic Geology, 63, [6], 655 (1968).

2) Maier, F. J., and Bellack, E., Fluorspar for Fluoridation. Journal of the American Water Works Association, 49, 41 (1957).

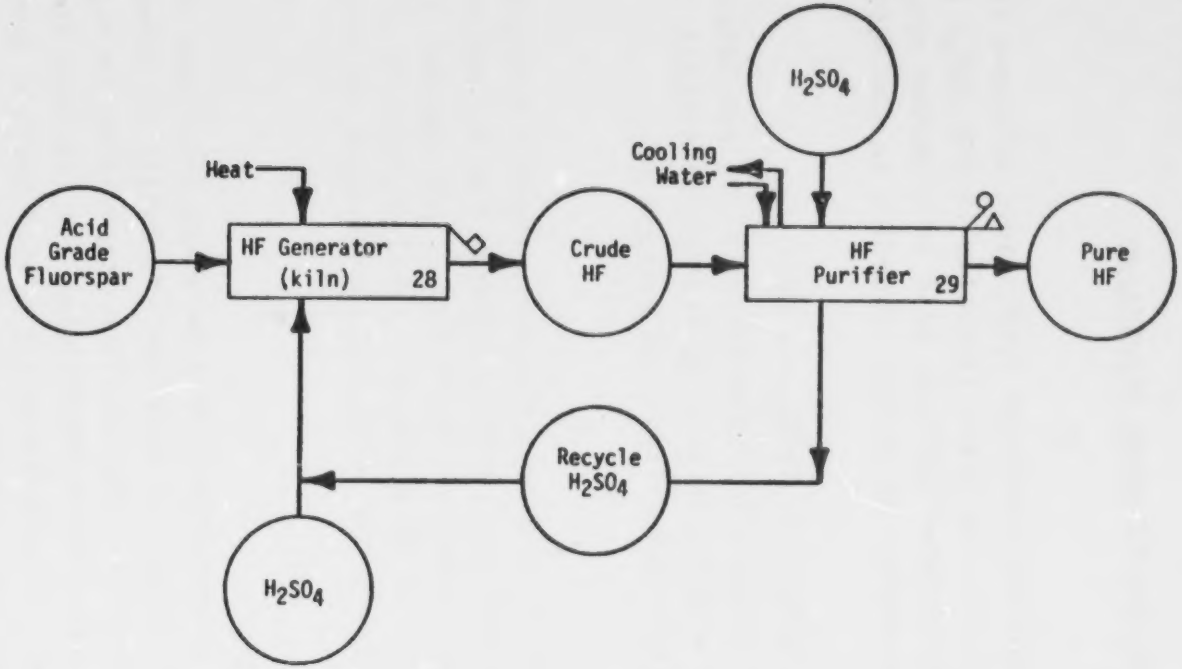

FIGURE 15. FLOWSHEET FOR THE PRODUCTION OF HYDROGEN FLUORIDE

Hydrogen Fluoride Generation

1. Function

To convert the mineral fluorspar (CaF_2) into hydrogen fluoride (HF). Finely ground acid grade fluorspar (≥ 97% CaF_2) is treated with concentrated sulfuric acid in a heated rotating steel kiln. The product is formed according to the following reaction:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\ HF$$

The anhydrous HF product is collected as a gas and later distilled to remove a small variety of foreign substances, e.g., compounds of silicon and sulfur (see process 29).

2. Input Materials

In the manufacture of hydrogen fluoride, about 2.4 metric tons of finely ground acid grade fluorspar and 2.7 metric tons of commercial 96-98% sulfuric acid (5-10% excess) are used per metric ton of HF produced. Small quantities of oleum are used to keep the concentration of H_2SO_4 at the 96-98% level.

3. Operating Parameters

Since the reaction between sulfuric acid and fluorspar is endothermic, heat is usually supplied externally by direct fire to the rotary kiln. The reaction temperature is kept at 200 to 250°C. Under these conditions, the reaction time is 30 to 60 minutes. A kiln 2 m x 4 m should produce about 200 kg. of hydrogen fluoride per hour. The overall yield of HF is about 90% based on fluorspar; and 80% based on H_2SO_4.

4. Utilities

Assuming a production rate of 200 kg. of HF per hour, an estimated 120,000 kcal./hr. of heat are required.

5. Waste Streams

The by-product from the HF production is calcium sulfate ($CaSO_4$). This is removed from the rotating kiln, at the end opposite the feed, via an air-lock screw drive and fed into water. This by-product can be neutralized with lime and is frequently discarded (ground burial) although it can be sold as gypsum or used in the manufacture of cements. Assuming a production rate of 200 kg./hr. of HF, about 775 kg./hr. of $CaSO_4$ are produced.

6. EPA Source Classification Code

3-01-012-02 ROTRYKILN W/OSCRUB

7. References

1) Bradbury, J. C., Finger, G. C., and Major, R. L., Fluorspar in Illinois, Illinois State Geological Survey Circular 420, 1968, Urbana, Illinois.

2) Encyclopedia of Technology, Kirk-Othmer 2nd Edition, Vol. 9, Interscience Publishers, New York, 1966 pp 610-625.

Hydrogen Fluoride Purification

1. Function

In this process crude HF is purified by a series of sorption, desorption and distillation steps which utilize sulfuric acid (H_2SO_4). The volatile impurities are separated by these steps and the impure HF is recovered from the H_2SO_4 as >99% pure HF. The towers and distillation apparatus needed to accomplish this can be made of steel.

2. Input Materials

The feed materials to this process are composed primarily of hydrogen fluoride, with small quantities of SO_2, SiF_4, CO_2, H_2SO_4, and H_2O. The feed entering this process from the kiln (process 28) is composed of about 95% HF, 4% air and 1% of the above impurities. Further downstream weak sulfuric acid is fed countercurrent to the main flow and acts as an absorbent for the hydrogen fluoride.

3. Operating Parameters

The product from the kiln is fed into this process at about 150°C where it is cooled with condensers to liquefy the HF. The cooled gases are passed into the H_2SO_4 scrubber and the HF and H_2O are absorbed into this solvent. The H_2SO_4 containing the HF is subjected to warming for removal by distillation of the >99% pure HF; the water remains behind with the H_2SO_4.

4. Utilities

Since the product gases entering this process are at temperatures of about 150°C, they need only be cooled to condense

the hydrogen fluoride (b.p. 19°C). Cooling water must remove about 375,000 kcal. of heat per metric ton of hydrogen fluoride produced.

5. **Waste Streams**

Gaseous HF and SiF_4 are scrubbed out of the vent gases with water to form H_2SiF_4, which is marketed as a 30-35% solution.

A gaseous effluent of SO_2 and CO_2 is vented to the air. The amounts of these gases which are vented will vary with the purity of the fluorspar used in process 28, but probably amount to less than 10 kg per metric ton of HF produced.

6. EPA Source Classification

3-01-012-01 ROTRYKILN W/SCRUB

7. References

1) Finger, G. C., Risser, H. E., and Bradbury, J. C., "Illinois Fluorspar," Illinois State Geological Survey Circular 296, 1960.

2) Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Vol. 9, Interscience Publishers, New York, 1966, pp 610-625.

APPENDIX A

RAW MATERIALS

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Table A-1. LIST OF RAW MATERIALS

acetic anhydride
acetyl fluoride
acetylene
antimony pentachloride
antimony trichloride
aromatic chlorocarbons, unspecified
bromine
carbon dioxide
carbon tetrabromide
carbon tetrachloride
chlorine
chloroform
dimethyl ether
ferrosilicon
fluorspar, ≥ 97% CaF_2
flotation agents, unspecified
hexanes
hexachloroacetone
hexachlorobutadiene
hydrocarbons, unspecified
hydrogen
hydrogen fluoride
iodine
methylene chloride
methyl sulfonyl fluoride
phosphorus pentoxide
potassium bifluoride
potassium fluoride
potassium permanganate
pyridine compounds, unspecified
pyrimidine compounds, unspecified
sodium fluoride
sodium hydroxide
sodium silicate
sulfuric acid
tetrachloroethylene
trichloroethylene
tri-n-butylamine

APPENDIX B

PRODUCTS AND BY-PRODUCTS

Table B-1. LIST OF PRODUCTS AND BY-PRODUCTS

bromotrifluoromethane
calcium sulfate
carbon dioxide
1-chloro-1,1-difluoroethane
chlorodifluoromethane
chloropentafluoroethane
chlorotrifluoroethylene
chlorotrifluoromethane
decafluorobutane
dibromodifluoromethane
1,2-dibromohexafluoropropane
1,2-dibromotetrafluoroethane
1,2-dichloro-1,1-difluoroethane
1,2-dichloro-1,2-difluoroethane
1,1-dichloro-2,2-difluoroethylene
1,2-dichloro-1,2-difluoroethylene
dichlorodifluoromethane
1,2-dichlorofluoroethane
dichlorofluoromethane
1,2-dichlorohexafluoropropane
1,2-dichlorotetrafluoroethane
1,1-difluoroethane
1,1-difluoroethylene
difluoromethane
difluoromethyl trifluoromethyl ether
fluoroethylene
fluorinated aromatic compounds, unspecified
fluorinated heterocyclic compounds, unspecified
fluosilicic acid
hexafluoroacetone
hexafluoroacetone, sesquihydrate
hexafluoroacetylacetone
hexafluorobutyne-2
hexafluorocyclobutene
hexafluoroethane

Table B-1 (Continued). LIST OF PRODUCTS AND BY-PRODUCTS

hexafluoroisopropanol
hexafluoropropylene
hydrogen bromide
hydrogen chloride, anhydrous
hydrochloric acid
1-iodoperfluorohexane
manganese dioxide
octafluorobutene-2
octafluorocyclobutane
octafluoropropane
pentafluoroethane
phosphoric acid
silicon tetrafluoride
silver iodide
sodium fluoride
sulfur dioxide
1,1,1,2-tetrachloro-2,2-difluoroethane
1,1,2,2-tetrachloro-1,2-difluoroethane
1,1,1,3-tetrachlorotetrafluoropropane
1,1,2,2-tetrafluoroethane
tetrafluoroethylene
tetrafluoromethane
trichlorofluoromethane
2,2,3-trichloroheptafluorobutane
1,1,2-trichloro-1,2,2-trifluoroethane
1,1,1-trichloro-2,2,2-trifluoroethane
1,1,1-trichloropentafluoropropane
trifluoroacetic acid
trifluoroacetic anhydride
1,1,1-trifluoroethane
1,2,2-trifluoroethane
trifluoroethanol
trifluoroethylene
trifluoroethyl vinyl ether
trifluoromethane
bis(trifluoromethyl) ether
trifluoromethyl iodide

APPENDIX C

PRODUCERS AND PRODUCTS

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Table C-1. COMPANY/PRODUCT LIST

Bromotrifluoromethane ($CBrF_3$)
- Du Pont

1-Chloro-1,1-difluoroethane ($CClF_2$-CH_3)
- Allied
- Du Pont
- Pennwalt

Chlorodifluoromethane ($CHClF_2$) (FC-22)
- Allied
- Du Pont
- Pennwalt
- Union Carbide
- Kaiser
- Racon

Chloropentafluoroethane ($CClF_2$-CF_3) (FC-115)
- Allied
- Du Pont

Chlorotrifluoroethylene ($CClF$=CF_2)
- Allied
- Hooker
- 3 M

Chlorotrifluoromethane ($CClF_3$) (FC-13)
- Allied
- Du Pont
- Pennwalt

Decafluorobutane (C_4F_{10})
- Phillips[1]

Dibromodifluoromethane (CBr_2F_2)
- Du Pont
- PCR[2]

1,2-Dibromohexafluoropropane ($CBrF_2$-$CBrF$-CF_3)
- Du Pont[3]

Table C-1 (Continued). COMPANY/PRODUCT LIST

1,2-Dibromotetrafluoroethane ($CBrF_2$-$CBrF_2$)
Du Pont

1,2-Dichloro-1,1-difluoroethane ($CClF_2$-CH_2Cl)
Phillips[1]

1,2-Dichloro-1,2-difluoroethane (CHClF-CHClF)
Phillips[1]
PCR

1,1-Dichloro-2,2-difluoroethylene (CCl_2=CF_2)
Allied
PCR

1,2-Dichloro-1,2-difluoroethylene (CClF=CClF)
Allied
PCR

Dichlorodifluoromethane (CCl_2F_2) (FC-12)
Allied
Du Pont
Kaiser
Pennwalt
Racon
Union Carbide

1,2-Dichlorofluoroethane (CHClF-CH_2Cl)
Phillips[1]

Dichlorofluoromethane ($CHCl_2F$) (FC-21)
Allied
Du Pont

1,2-Dichlorohexafluoropropane ($CClF_2$-CClF-CF_3)
Du Pont[3]

Table C-1 (Continued). COMPANY/PRODUCT LIST

1,2-Dichlorotetrafluoroethane ($CClF_2$-$CClF_2$) (FC-114)
- Allied
- Du Pont
- Union Carbide[4]
- Pennwalt[4]

1,1-Difluoroethane (CHF_2-CH_3)
- Allied
- Du Pont

1,1-Difluoroethylene (CF_2=CH_2) (Vinylidene fluoride)
- Allied
- Du Pont

Difluoromethyl trifluoromethyl ether (CHF_2-O-CF_3)
- Phillips[1]

Fluoroethylene (CHF=CH_2) (Vinyl fluoride)
- Du Pont

Fluorinated Aromatic Chemicals (unspecified)
- Olin

Fluorinated Heterocyclic Chemicals (unspecified)
- Olin

Hexafluoroacetone (CF_3-CO-CF_3)
- Allied[5]
- Du Pont
- Matheson[5]
- PCR[5]
- Phillips[1]

Table C-1 (Continued). COMPANY/PRODUCT LIST

Hexafluoroacetone, sesquihydrate (CF_3-CO-CF_3 · 1½ H_2O)
Du Pont

Hexafluoroacetylacetone (CF_3-CO-CH_2-CO-CF_3)
PCR

Hexafluorobutyne-2 (CF_3-C≡C-CF_3)
PCR

Hexafluorocyclobutene (F)
PCR

Hexafluoroethane (CF_3-CF_3) (FC-116)
Du Pont

Hexafluoroisopropanol (CF_3-CHOH-CF_3)
Du Pont

Hexafluoropropylene (CF_3-CF=CF_2)
Du Pont
PCR[5]

1-Iodoperfluorohexane (CF_2I-CF_2-CF_2-CF_2-CF_2-CF_3)
Du Pont
Thiokol

Octafluorobutene-2 (CF_3-CF=CF-CF_3)
Halocarbon [5]

Octafluorocyclobutane (F) (FC-C318)
Du Pont[3]
Phillips[1]

Table C-1 (Continued). COMPANY/PRODUCT LIST

Octafluoropropane (CF_3-CF_2-CF_3)
- Phillips[1]

Pentafluoroethane (CHF_2-CF_3)
- PCR
- Phillips[1]

1,1,1,2-Tetrachloro-2,2-difluoroethane (CCl_3-$CClF_2$)
- Allied[5]
- Du Pont[5]

1,1,2,2-Tetrachloro-1,2-difluoroethane (CCl_2F-CCl_2F) (FC-112)
- Allied[5]
- Du Pont[5]
- Union Carbide[4]

1,1,1,3-Tetrachlorotetrafluoropropane (CCl_3-CF_2-$CClF_2$)
- Du Pont[3]

1,1,2,1-Tetrafluoroethane (CHF_2-CHF_2)
- Phillips[1]

Tetrafluoroethylene (CF_2=CF_2)
- Du Pont
- Pennwalt[5]
- Thiokol[5]

Tetrafluoromethane (CF_4) (FC-14)
- Du Pont

Trichlorofluoromethane (CCl_3F) (FC-11)
- Allied
- Du Pont
- Pennwalt
- Union Carbide

Table C-1 (Continued). COMPANY/PRODUCT LIST

2,2,3-Trichloroheptafluorobutane (CF_3-CCl_2-CClF-CF_3)
- Halocarbon Products[5]

1,1,2-Trichloro-1,2,2-trifluoroethane (CCl_2F-$CClF_2$) (FC-113)
- Allied
- Du Pont
- Kaiser
- Pennwalt
- Racon
- Union Carbide

1,1,1-Trichloro-2,2,2-trifluoroethane (CCl_3CF_3)
- Allied[6]
- Du Pont[6]
- PCR[4]

1,1,1-Trichloropentafluoropropane (CCl_3-CF_2-CF_3)
- Du Pont[3]

Trifluoroacetic Acid (CF_3COOH)
- Halocarbon Products
- Phillips[1]

Trifluoroacetic Anhydride (CF_3CO-O-CO-CF_3)
- Halocarbon Products

1,1,1-Trifluoroethane (CF_3-CH_3)
- Phillips[1]

1,2,2-Trifluoroethane (CH_2F-CHF_2)
- Phillips[1]

Table C-1 (Continued). COMPANY/PRODUCT LIST

Trifluoroethanol (CF_3CH_2OH)
Halocarbon Products
Trifluoroethylene ($CHF=CF_2$)
PCR
Trifluoroethyl vinyl ether (CF_3-CH_2-O-$CH=CH_2$)
Airco, Inc.
Trifluoromethane (CHF_3) (FC-23)
Allied
Du Pont
bis(Trifluoromethyl) ether (CF_3-O-CF_3)
Phillips[1]
Trifluoromethyl iodide (CF_3I)
PCR

1) Pilot plant only - now discontinued.
2) Possible distributor only.
3) Not currently in production - telecon.
4) Probable producer not listed in 1976 DCP.
5) Possibly not in current production.
6) Not made as a pure product.

Table C-2. PRODUCERS OF FLUOROCARBONS

Company	Annual Capacity (millions of kg)
E. I. du Pont de Nemours & Co.	
Organic Chemicals Department	
Freon Products Division	
Antioch, California Deepwater, New Jersey East Chicago, Indiana Louisville, Kentucky Montague, Michigan	230
Allied Chemical Corporation	
Specialty Chemicals Division	
Baton Rouge, Louisiana Danville, Illinois Elizabeth, New Jersey El Segundo, California	140
Union Carbide Corporation	
Chemicals and Plastics Div.	
Institute & South Charleston, West Virginia	70
Pennwalt Corporation	
Chemical Division	
Calvert City, Kentucky Thorofare, New Jersey	53
Kaiser Aluminum & Chemical Corp.	
Kaiser Chemicals Division	
Gramercy, Louisiana	23
Racon Incorporated	
Wichita, Kansas	9

Table C-3. SPECIALITY FLUOROCHEMICALS LIST

Airco, Inc.
Ohio Medicap Products Division
Cleveland, Ohio

Halocarbon Products Corporation
82 Burlews Court
Hackensack, New Jersey 07601

Hooker Chemical Corporation
Specialty Chemicals Division
Niagara Falls, New York 14302

Matheson Gas Products
Post Office Box E.
Lyndhurst, New Jersey 07071

3 M Company
Commercial Chemicals Division
3 M Center
Saint Paul, Minnesota, 55101

Olin Corporation
120 Long Ridge Road
Stamford, Connecticut 06904

*Phillips Petroleum Company
Chemical Dept./Commercial Development Division
Bartlesville, Oklahoma 74004

PCR, Inc.
Gainesville, Florida

Thiokol Chemical Corporation
P. O. Box 1296
Trenton, New Jersey 08607

*Produced on a pilot plant basis only - subsequently discontinued

Table C-4. PRODUCERS OF HYDROGEN FLUORIDE

Company	Annual Capacity (metric tons)
Allied Chemical Corporation Industrial Chemicals Division Baton Rouge, Louisiana Geismar, Louisiana Nitro, West Virginia North Claymont, Delaware Pittsburg, California	98,000
E. I. du Pont de Nemours & Co., Inc. Biochemicals Department LaPorte, Texas	91,000
Aluminum Company of America Point Comfort, Texas	50,000
Kaiser Aluminum & Chemical Corporation Kaiser Chemicals Division Grammercy, Louisiana	45,000
Pennwalt Corporation Chemical Division Calvert City, Kentucky	23,000
Stauffer Chemical Company Industrial Chemical Division Greens Bayou, Texas	16,000
Kewanee Oil Company Harshaw Chemical Company, Division Industrial Chemicals Department Cleveland, Ohio	16,000

Table C-4 (Continued). PRODUCERS OF HYDROGEN FLUORIDE

Olin Corporation Industrial Products and Services Division Joliet, Illinois	12,000
Essex Chemical Corporation Chemicals Division Pausboro, New Jersey	10,000
Lehigh Valley Chemical Company Glendon, Pennsylvania	4,000
Total	361,000

Source: Chemical Marketing Reporter 7/15/73 p. 1.